science for a changing world

Knowledge Gaps and Opportunities in Water-Quality Drivers of Aquatic Ecosystem Health

Open-File Report 2023–1085

U.S. Department of the Interior
U.S. Geological Survey

Cover. Alpine stream near the historical mining town of Leadville, Colorado. Photograph by Jud Harvey, U.S. Geological Survey.

Knowledge Gaps and Opportunities in Water-Quality Drivers of Aquatic Ecosystem Health

Edited by Judson W. Harvey, Christopher H. Conaway, Mark M. Dornblaser, Allen C. Gellis, A. Robin Stewart, and Christopher T. Green

Open-File Report 2023–1085

U.S. Department of the Interior
U.S. Geological Survey

U.S. Geological Survey, Reston, Virginia: 2024

Suggested citation:
Harvey, J.W., Conaway, C.H., Dornblaser, M., Gellis, A., Stewart, A.R., and Green, C.T., eds., 2024, Knowledge Gaps and Opportunities in Water-Quality Drivers of Aquatic Ecosystem Health: U.S. Geological Survey Open-File Report 2023–1085, 72 p., https://doi.org/10.3133/ofr202231085.

ISSN 2331-1258 (online)

Abstract

This report identifies key scientific gaps that limit our ability to predict water quality effects on health of aquatic ecosystems and proposes approaches to address those gaps. Topics considered include (1) coupled nutrient-carbon cycle processes and related ecological-flow-regime drivers of ecosystem health, (2) anthropogenic and geogenic toxin bioexposure, (3) fine sediment drivers of aquatic ecosystem health, and (4) freshwater salinization. Each topic is addressed in terms of scientific gaps, approaches, and timelines to help guide portions of the U.S. Geological Survey Water Mission Area (https://www.usgs.gov/mission-areas/water-resources) research portfolio and other national research efforts. The report provides an assessment of several of the major challenges and opportunities concerning water quality impacts on aquatic ecosystem health. It will be important to maintain broad-based expertise and flexibility to address the full range of long-term water quality issues facing the Nation’s water resources.

Acknowledgments

The report was produced as a part of the National Gap Analysis of Water-Quality Understanding and Predictive Capabilities project for the U.S. Geological Survey (USGS). This knowledge and data gap analysis reflects the individual and collective efforts of the authors working in concert with many other project members and colleagues. Although its content is the responsibility of the authors the hope is that it reflects the many viewpoints shared with us by agency scientists during the discussion and review phases of the project. Foremost, we are indebted to the reviewers of our draft for their insightful comments and follow-up discussion, including Peter Van Metre, Larry Barber, Joanna Blake, Barbara Bekins, J.K. Böhlke, Se Jong Cho, Melinda Erickson, Zachary Johnson, Yousif Kharaka, Noah Knowles, Blaine McCleskey, Christopher Mebane, Lisa Nowell, Gretchen Oelsner, Christine Rumsey, Dale Robertson, and Ted Stets. Thanks also to Barbara Bekins for her supportive co-leadership of the Water Quality Gaps project, Melinda Erickson and contractor Tea Jackson-Strong for their expert assistance in formatting, Kathryn Pauls for editing, Kimber Petersen for illustration support, and Cory Hurd for layout.

Contents

Abstract iii
Acknowledgments iv

Chapters

A. Framework for a Gap Analysis of Aquatic Ecosystem Health 1

By Judson W. Harvey, Mark M. Dornblaser, A. Robin Stewart, Allen C. Gellis, Christopher H. Conaway, Nancy T. Baker, Jeramy R. Jasmann, Deborah A. Repert, Richard L. Smith, Elizabeth J. Tomaszewski, and Kimberly P. Wickland

Introduction 1
What is Aquatic Ecosystem Health? 1
How is Aquatic Ecosystem Health Assessed? 2
Federal Agency Role in Aquatic Ecosystem Health 3
Gaps in Understanding of Water Quality Threats to Aquatic Ecosystem Health 3
How a Gap Analysis Can Serve the USGS 3
Potential Topics for an Eco-Health Gap Analysis 4
Selected Topical Areas for the Gap Analysis 5
References Cited 5

B. Coupled Nutrient-Carbon Cycle Processes and Related Ecological-Flow Drivers of Aquatic Health 9

By Mark M. Dornblaser, Kimberly P. Wickland, Deborah A. Repert, Richard L. Smith, and Judson W. Harvey

Statement of the Problem 9
Status of Knowledge and Key Limitations 10
Priority Knowledge Gaps in Coupled Nutrient-Carbon Processes Affecting Ecological Health 12
Gap 1. Multi-factor Nitrogen, Phosphorus, and Labile Carbon Sources Interacting with Eco-Flow Drivers 12
Spatial and Temporal Distributions of Labile Organic C Sources and Their Role in Coupled C-N-P Metabolic Reactions 12
Relation Between Watershed Carbon, Nitrogen, and Phosphorus Biogeochemical Processes and Development of Harmful Algal Blooms 12
Beyond Streamflow for Prediction of Ecologically Relevant Flow and Physical Metrics 13
Gap 2. Redox Processes Controlling Storage, Processing, and Release of N, P, Fe, As, and Other Contaminants 13
Nitrogen, Phosphorus, Iron, and Arsenic Interactions in Wastewater and Septage Disposal 13
Gap 3. Interaction Between Nutrient Cycles and Contaminants of Emerging Concern 13
Effects of Antibiotics (Domestic and Agricultural) on Water and Sediment Biogeochemistry and Co-Contaminant Fate and Transport 13
Interaction Between Nitrogen Cycle Processes and Contaminants of Emerging Concern 14
Effect of Microplastics on Carbon, Nitrogen, and Phosphorus Biogeochemical Processes 14
Approaches to Address Gaps in Coupled Processes Affecting Water Availability 14

Microbial Profiling 14
Mechanistic Studies of Coupled Processes 16
Comprehensive Measurements of Coupled Constituents at Fixed Stations....................16
Mapping of Nitrogen, Phosphorus, Carbon, and Related Eco-Flow Metrics Across Multiple Scales 16
Timelines....................17
Near-Term (2-Year) Advancements 17
Mid-Term (2- to 5-Year) Advancements 19
Long-Term (10-Year) Advancements 19
Expected Outcomes....................19
References Cited....................20

C. Anthropogenic and Geogenic Contaminant Bioexposures Affecting Aquatic Ecosystems 27

By A. Robin Stewart, Jeramy R. Jasmann, Elizabeth J. Tomaszewski, and Judson W. Harvey

Purpose and Scope 27
Statement of the Problem....................27
Status of Knowledge and Key Limitations 29
Anthropogenic Contaminants....................30
Geogenic Contaminants 30
Priority Gaps in Anthropogenic and Geogenic Bioexposures 31
Anthropogenic Wastewater Contaminants of Emerging Concern Gaps....................31
Gap 1. Major Factors Affecting Human and Aquatic Organism Health....................32
Wastewater Discharge and Toxicity Benchmark Data 32
Biogeochemical Model Parameters....................32
Gap 2. Water Quality Assessment Tools for Aquatic Organism and Human Health Risk....................33
Develop Risk Prioritization Scheme....................33
Develop Tools for Screening-Level Contaminant of Emerging Concern Assessments....................34
Geogenic Contaminant Gaps 34
Gap 3. Mechanistic Understanding of Uptake Dynamics of Geogenic Contaminants for Watershed Assessments of Risk and Coupled Hydrologic-Biogeochemical Model Development 34
Biogeochemical Controls on Chemical Speciation....................35
Chemical Speciation Controls on Particulate Adsorption and Bioaccumulation 35
Assimilation of Geogenic Contaminants from Inorganic and Organic Particles....................36
Hydrologic Controls on Chemical Speciation and Particulate Bioavailability....................36
Gap 4. Bioavailability and Toxicity of Organometallic Complexes....................36
Bioexposure Studies of Metal-Dissolved Organic Matter Complexes with Organisms at the Base of the Food Web....................36
Timelines....................37
Expected Outcomes....................38
References Cited....................39

D. Fine Sediment Drivers of Aquatic Ecosystem Health 45
By Allen C. Gellis, Judson W. Harvey, Christopher H. Conaway, and Nancy T. Baker
Purpose and Scope 45
Statement of the Problem....45
Status of Knowledge and Capabilities Including Key Gaps and Limitations 46
Sediment-Associated Transport of Constituents....50
Managing Fine Sediment....51
Gaps in Fine Sediment Drivers and Associated Contaminants....52
Gap 1. Understanding Fine Sediment Sources and Connectivity Through the Nation's Waterways 52
Gap 2. How Fine Sediment Sources are Apportioned Between Erosion in Channel Corridor Versus Uplands 52
Gap 3. Predicting Fine Sediment-Associated Contaminants and Biophysical Drivers of Eco-Health....53
Gap 4. Ability to Forecast Climate and Land-Use Driven Alterations of Fine Sediment.53
Addressing Gaps—Approaches and Priorities 53
Tracing Sediment Sources....53
Modeling Fine Sediment Dynamics and Associated Contaminants 54
Timelines....55
Near-Term (2 Years)....55
Mid-Term (2–5 Years) 55
Long-Term (10 Years)....55
References Cited....56
E. Freshwater Salinization—An Expanding Impairment of Aquatic Ecosystem Health....63
By Christopher H. Conaway, Nancy T. Baker, Judson W. Harvey, and Allen C. Gellis
Purpose and Scope 63
Statement of the Problem....63
Status of Knowledge and Key Limitations 64
Radionuclides....65
Knowledge Gaps in Salinity Drivers of Ecosystem Health....67
Gap 1. Defining the Chemical Landscape of Salinization....67
Gap 1a. Predicting and Understanding Changes in Salinity....67
Gap 1b. Salinity Loadings and Pathways....68
Gap 2. Evaluating Ecosystem Risks from Salinization 68
Gap 2a. Salinity Mobilization of Chemical Cocktails (Mixtures) 68
Gap 2b. Effects of Sea Level Rise on Coastal Ecosystems....69
Gap 2c. The Effects of Salinization on Changing Community Structure (From Microbes to Harmful Algal Blooms to Invasive Species)....69
Priorities and Timelines for Addressing Gaps....69
Priorities 69
Gap 1a. Predicting and Understanding Changes in Salinity....69
Gap 1b. Salinity Loadings and Pathways....69
Gap 2a. Salinity Mobilization of Chemical Cocktails (Mixtures) 69
Gaps 2b and 2c. Sea Level Rise, Salinization, and Changing Community Structure....69
Timelines....70
Near-Term (2–5 Years)....70
Mid- to Long-Term (5–10 Years)....70
References Cited....70

Figures

A1. Diagrams of aquatic ecosystem health assess the structure and function of biological communities responding to physical and chemical factors and biological needs and tolerances 2
B1. Diagram of coupled nutrient-carbon processes and their effect on aquatic eco-health.... 10
C1. Drivers and mechanisms of bioexposure of contaminants in aqueous ecosystems illustrating different ways contaminants enter the food web and the factors influencing uptake and trophic transfer 29
C2. Diagram of a proposed U.S. Geological Survey integrated interdisciplinary, cross-mission-area approach to deliver actionable water-availability science to address complex processes and mechanisms for solving knowledge gaps in anthropogenic and geogenic contaminant bioexposures affecting aquatic ecosystems 38
D1. Diagram of drivers, sources, and storages of fine sediment and particle-associated contaminants affecting aquatic ecosystems and the four principal knowledge gaps identified by the U.S. Geological Survey for fine sediment drivers of aquatic ecological health 46
D2. Flow diagram of the components in the sediment total maximum daily load procedure....52
E1. Diagram of sources and drivers of freshwater salinization with potential ecological health impairments. 64

Tables

A1. Opportunities for the U.S. Geological Survey Water Mission Area in aquatic ecosystem health 4
B1. Summary of nutrient-carbon constituents, relevance to aquatic ecosystem health, and previous findings from the U.S. Environmental Protection Agency rankings (2017)....11
B2. Summary of prioritized U.S. Geological Survey knowledge gaps, approaches, and expected outcomes for water quality drivers of aquatic ecosystem health 15
B3. Timeline summary of prioritized U.S. Geological Survey approaches to closing knowledge gaps for coupled nutrient-carbon cycle processes and related ecological-flow drivers of aquatic health....18
C1. The four major bioexposure knowledge gaps of water quality drivers of aquatic ecosystem health identified by the U.S. Geological Survey, grouped by anthropogenic contaminants of emerging concern or geogenic contaminant class....28
C2. Timeline summary of prioritized U.S. Geological Survey approaches to closing knowledge gaps for the anthropogenic and geogenic contaminant bioexposures affecting aquatic ecosystems 37
D1. Summary of fine sediment knowledge gaps, including background rationale, metrics, modeling, and key references for water-quality drivers of aquatic ecosystem health identified by the U.S. Geological Survey 47
D2. Drivers and indicators of fine sediment dynamics and related physicochemical controls of aquatic ecosystem health....49
E1. Summary table for freshwater salinity gap analysis for aquatic ecosystem health identified by the U.S. Geological Survey and grouped by chemical salinization and ecosystem risks from salinization....65
E2. Single-factor constituents of concern, drivers, and indicators of aquatic ecosystem health identified by the U.S. Geological Survey 66

Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
cubic mile (mi^3)	4.168	cubic kilometer (km^3)
billion gallons (Ggal)	0.003785	cubic kilometer (km^3)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	metric ton (t)

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
liter (L)	0.2642	gallon (gal)
cubic kilometer ($km^{3)}$	2.64172	billion gallon (Ggal)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
metric ton (t)	1.102	ton, short [2,000 lb]

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as °F = (1.8 × °C) + 32.

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as °C = (°F – 32) / 1.8.

Supplemental Information

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

ACCWW	USGS accumulated wastewater ratio in-line mapper
AGC	anthropogenic and geogenic contaminants
BAC	bioaccumulation coefficients
BCF	bioconcentration factors
BLM	biotic ligand model
CCC	criterion continuous concentration
CEC	contaminant of emerging concern
CMC	criterion maximum concentration
CWA	Clean Water Act
DART	decision analysis by ranking techniques
DDT	dichlorodiphenyltrichloroethane
DNA	deoxyribonucleic acid
DOC	dissolved organic carbon
DOE	U.S. Department of Energy
DOM	dissolved organic matter
EC	efficiency concentration
EPA	U.S. Environmental Protection Agency
EPI	EPA Estimation Parameter Interface Suite
FDA	U.S. Food and Drug Administration
FERC	Federal Energy Regulatory Commission
FIAM	free ion activity model
FPOM	fine particulate organic matter
GIS	geographic information system
HAB	harmful algal bloom
IRB	Illinois River Basin
IWP	USGS WMA Integrated Water Prediction program
IWAAS	USGS WMA Integrated Watershed Availability Assessments Program
IWS	USGS Integrated Water Science
Kd	distribution coefficient
Koc	carbon-water coefficient

Kow	octanol-water coefficient
LC	lethal concentration
MeHg	methylmercury
μm	micrometer
MMI	macroinvertebrate multimetric index
NASA	National Aeronautics and Space Administration
NGWOS	USGS Next Generation Water Observing Stations
NOAA	National Oceanic and Atmospheric Administration
NOEC	no observed effect concentration
NWQP	USGS National Water Quality Program
OC	organic carbon
OMP	organic micropollutant
PAH	polycyclic aromatic hydrocarbons
PFAS	per- and polyfluoroalkyl substances
PNEC	predicted no effect concentration
POC	particulate organic carbon
QSAR	quantitative structure-activity relationship
RNA	ribonucleic acid
RSQA	USGS Regional Stream Quality Assessment
SSC	suspended-sediment concentration
TDS	total dissolved solid
TMDL	total maximum daily load
TN	total nitrogen
TP	total phosphorus
TSS	total suspended solids
USACE	U.S. Army Corps of Engineers
USDA	U.S. Department of Agriculture
USGS	U.S. Geological Survey
WMA	USGS Water Resources Mission Area
WWTP	wastewater treatment plant

Knowledge Gaps and Opportunities in Water-Quality Drivers of Aquatic Ecosystem Health
Edited by Judson W. Harvey, Christopher H. Conaway, Mark M. Dornblaser, Allen C. Gellis, A. Robin Stewart, and Christopher T. Green
[Also see https://doi.org/10.3133/ofr20231085]

Chapter A

Framework for a Gap Analysis of Aquatic Ecosystem Health

By Judson W. Harvey, Mark M. Dornblaser, A. Robin Stewart, Allen C. Gellis, Christopher H. Conaway, Nancy T. Baker, Jeramy R. Jasmann, Deborah A. Repert, Richard L. Smith, Elizabeth J. Tomaszewski, and Kimberly P. Wickland

Introduction

Gaps in scientific knowledge limit our ability to predict water quality effects on the health of aquatic ecosystems. This report summarizes key gaps and describes approaches to address them. In 2020 the Eco-Health Gap Analysis team for the USGS Water Resources Mission Area's National Water Quality Program (NWQP; https://www.usgs.gov/programs/national-water-quality-program) discussed potential topical areas. The following four key topical areas were selected for an in-depth gap analysis of water-quality drivers of aquatic ecosystem health and make up the remaining chapters of this report: coupled nutrient-carbon cycle processes and related ecological-flow drivers (Chapter B), anthropogenic and geogenic contaminant bioexposures (Chapter C), fine sediment drivers (Chapter D), and freshwater salinization (Chapter E). In each chapter, there is a discussion of the scientific gaps, approaches, and timelines to address the gaps.

What is Aquatic Ecosystem Health?

Many factors control the structure, function, and persistence of aquatic communities. Healthy aquatic ecosystems are characterized by flow and habitat conditions, water quality, and food availability that sustain the biological community close to the state of an undisturbed "reference community" (Baldaccini and others, 2009; Durbecq and others, 2020). Well-functioning river corridors often include naturally varying flows, geomorphic complexity, and diverse sediment conditions. Also important are appropriate levels of light, organic matter inputs, and other factors that support feeding, dispersal, nesting, and rearing of aquatic consumers. Refugia provide a buffer from excessive predation, extreme flows, and physiochemical stressors.

Natural aquatic communities undergo a variety of chemical, biological, and hydrological disturbances. Chemical disturbances include excessive inputs of salinity, toxic elements, fine sediment, organic matter, or nutrients from the watershed or corridor. Biological disturbances may stem from extended periods of low dissolved oxygen (Blaszczak and others, 2022) and high temperature (Briggs and others, 2018) that impose physiological stress, as well as whole-system disruptions of aquatic metabolism that include excessive, oxygen-depleting algal blooms (Glibert and others, 2010), blooms that are toxic (Burford and others, 2020), or blooms of undesirable species that are less nutritious for higher trophic levels (Giblin and others, 2022). Another major cause of biological disturbances is invasive species that out-compete native species and disrupt food webs. Hydrologic disturbances include changes to the natural flow regime (Poff and others, 1997) and to the natural sediment regime (Wohl and others, 2015) stemming from more frequent or ill-timed floods and droughts as well as changing seasonal patterns of high and low flows. Natural aquatic communities typically can recover from temporary levels of moderate stress. However, hydrologic disturbances may interact with chemical and biological disturbances to compound and prolong the effects on ecosystems.

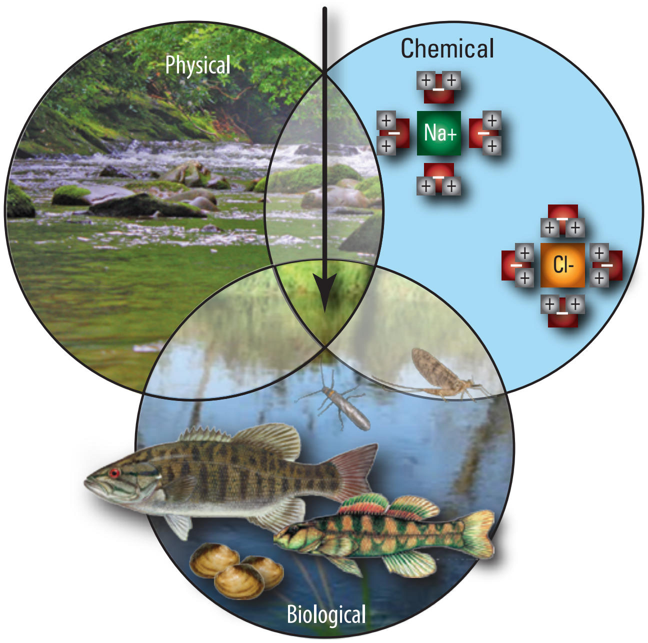
Human alteration of aquatic systems is increasing the occurrence and persistence of stressors. Industrial and agricultural activities have radically changed the global amount and distribution of atmospheric carbon dioxide (CO_2) (Canadell and others, 2007), reactive nitrogen (N) in the biosphere (Galloway and others, 2008), and distribution of phosphorus (P) (Gilbert, 2009), leading to reorganization of biological communities (Finzi and others, 2011). Extreme events related to climate change (for example, wildfires, floods, and droughts) interact with local land-use practices to influence concentrations of salinity and anthropogenic and geogenic contaminants, leading to negative impacts on aquatic ecosystems (Kolpin and others, 2002; Barnes and others, 2008; Focazio and others, 2008; Chapman and others, 2010; Bradley and others, 2016; Kaushal and others, 2018). Human-altered runoff regimes that increase the frequency of floods and droughts also may eliminate favorable sub-habitats and expose aquatic organisms to higher concentrations of contaminants. Land use effects are of particular concern where they influence flow, sediment sources, riparian shading, and the biogeochemistry of headwater streams as well as the larger river channels. Important functions of streams and rivers are enabled by interactions with subsurface hyporheic zones and with riparian zones and floodplains, elements that together with the main channel comprise the river corridor (Harvey and others, 2019). River corridor interactions collectively influence a broad array of water quality and aquatic ecosystem functions (Gilliam 1994; Wohl and others, 2015; Golden and Hoghooghi, 2017; Lynch and others, 2019; Harvey and others, 2019). Flow alterations and land use changes influence longitudinal and lateral connectivity of river corridors, capacity of riparian buffers for water purification, bank erosion and sediment supply, and hyporheic and riparian ecosystem functions that facilitate the storage and transformation of organic matter, nutrients, fine particulates, and contaminants (Wymore and others, 2023).

How is Aquatic Ecosystem Health Assessed?

Physical, chemical, and biological factors act together to influence the structure and function of aquatic communities (Carlisle and others, 2013) (fig. A1). Consequently, despite efforts to build simple criteria based on single factors, such as nutrient concentrations that specify eutrophication (for example, Dodds and Smith, 2016) or flow statistics that quantify flow alteration (for example, Poff and others, 2010), the signature of a healthy aquatic system is in fact quite difficult to assess. An alternative is to use an integrative metric that broadly characterizes aquatic health. For example, benthic macroinvertebrates in streams play a key role in processing detritus and providing food for higher consumers in healthy aquatic ecosystems. Sampling the benthos in thousands of streams provided the data for a macroinvertebrate multimetric index (MMI) that assesses health based on taxonomic richness, diversity, balance among feeding groups and habitat requirements, and pollution tolerance relative to reference streams (U.S. Environmental Protection Agency [EPA], 2020b). The resulting MMI provides a transferable measure of ecosystem health that is temporally persistent and can be consistently applied across the Nation. Other biological indicators also are used, for example, fish community metrics, as well as physiochemical indicators (nutrients, salinity, temperature), and physical habitat indicators (for example, riparian condition, excess fine sediment) (EPA, 2020b).

Aquatic ecosystem health is also assessed in terms of societal interests in the services and beneficial uses that are accrued. Scientific information can inform decisions by stakeholders and support investments to protect or enhance those valuable services. Ecosystem services are evaluated according to the functions performed, including water storage and purification, biological production and fisheries, biodiversity, carbon storage, recreational opportunities, and values of public natural spaces and private lands (Brauman and others, 2007). Stakeholder interest may range broadly from managing declines in specific biological communities (for example, endangered fisheries), managing water supply for human beneficial use while also reserving flows for biological

A. **Aquatic Ecosystem Health**



B

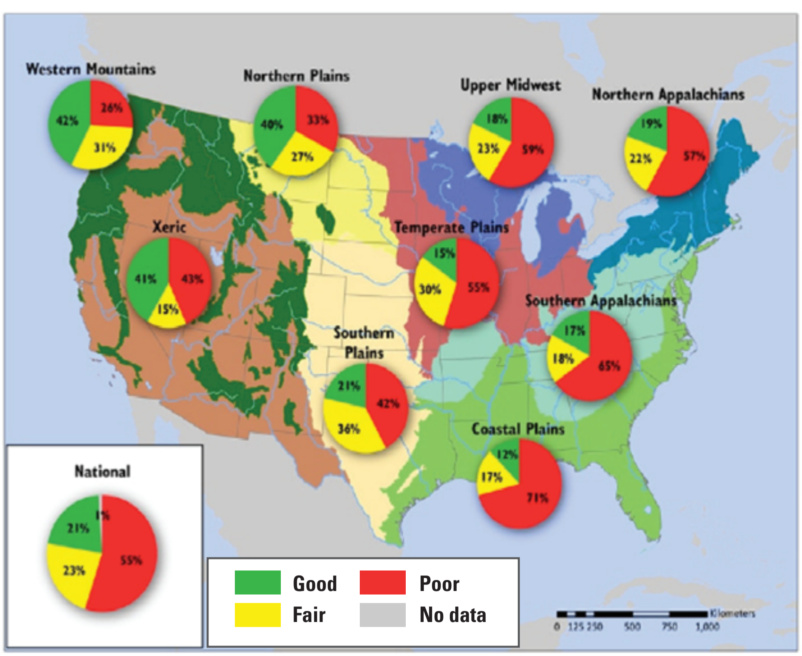


Figure A1. Diagrams of aquatic ecosystem health assess the structure and function of biological communities responding to physical and chemical factors and biological needs and tolerances. *A*, Venn diagram of physical, chemical, and biological factors acting together to influence the structure and function of aquatic communities (Carlisle and others, 2013). *B*, Multi-factor measures such as macroinvertebrate multimetric index (MMI) indicate that more than half of the stream miles in the continental United States rate as being in poor ecological condition, as shown in pie diagrams against mapped U.S. Environmental Protection Agency (EPA) level II ecoregions. The highest ecological impairment occurs in the Coastal Plain ecoregion (71 percent [%]) and lowest in the Western Mountains ecoregion (26%). Modified from EPA (2020b). Na^+, sodium cation; Cl^-, chlorine anion.

communities, managing contaminant loads to protect biological communities and sustain recreational uses, as well as managing waterways to address concerns about odor and aesthetic appeal.

Federal Agency Role in Aquatic Ecosystem Health

A summary understanding of the U.S. Geological Survey's (USGS's) mission among Federal agencies is the basis from which to begin knowledge gap analyses. Throughout the fall of 2020 the Eco-Health Gap Analysis team for the USGS Water Mission Area's National Water Quality Program (NWQP; https://www.usgs.gov/programs/national-water-quality-program) discussed potential topical areas. Scientific guidance in water quality and ecosystem health issues for the United States comes from Federal agencies such as the U.S. Environmental Protection Agency (EPA), USGS, U.S. Department of Agriculture (USDA), National Oceanic and Atmospheric Administration (NOAA), U.S. Department of Energy (DOE), U.S. Army Corps of Engineers (USACE), National Aeronautics and Space Administration (NASA), Federal Energy Regulatory Commission (FERC), and the National Science Foundation (NSF). The role of the USGS and other agencies is to carry out the necessary monitoring, laboratory-based experiments and modeling required to create the best framework to guide regulatory agencies, States and municipalities, non-governmental organizations (NGOs), and other stakeholders in their decision-making about water resources. This vitally important role is intended to ensure that regulations and best management practices are effective, including the protection of ecosystem health.

The scientific information provided by Federal agencies is used to design and implement protective management actions. Regulatory responsibilities are primarily in the EPA, FERC, and the USACE which have regulatory authority over wastewater releases and physical alteration of waterways, as well as river and reservoir infrastructure and operations. The EPA tracks and compiles State reporting of water quality impairments of waterways (EPA, 2017) and has established exceedance criteria for contaminants to protect aquatic organisms. Many of those criteria target specific organisms and life stages to protect against contaminants such as pesticides, metals, and emerging contaminants. Notably, many of EPA's exceedance thresholds for specific compounds are lower for ecological health than for human beneficial use.

Declines in aquatic ecosystem health are often the result of multiple factors. For example, the biological impairment of benthic macroinvertebrate communities is often related to nutrients, salinity, and temperature, but is almost twice as likely to be rated poor when levels of excess fine sediment are high (EPA, 2020a). Federal agency programs such the USGS Water Resources Mission Area (WMA) Regional Stream Quality Assessment Program (RSQA, https://www.usgs.gov/tools/regional-stream-quality-assessment-rsqa) have demonstrated how the dominant physical and water-quality drivers of aquatic health can be identified. For example, alteration of streamflow, particularly in the western United States, often is found to operate in concert with water-quality drivers to impair ecological health (Carlisle and others, 2013). Identifying the multiple, key factors controlling aquatic health is imperative to serve stakeholders charged with decisions and investments to protect ecological resources across the Nation.

Gaps in Understanding of Water Quality Threats to Aquatic Ecosystem Health

How a Gap Analysis Can Serve the USGS

Presently the USGS WMA focuses on measuring water flow and water quality in a nationally consistent manner to support stakeholder information needs to manage water resources. In addition to making the measurements, the USGS analyzes spatial and temporal trends and models source areas and movement of constituents of concern to receiving waters. Furthermore, the USGS characterizes hydrologic alterations of streamflow and its role in structuring aquatic communities. USGS also interacts directly with local stakeholders that support specific stakeholder interests in current programs and priorities.

USGS's expertise in hydrologic flows, constituent source areas, and movement of constituents through watersheds does not serve all stakeholder needs, especially from an ecosystems health perspective. Quantifying source areas and loads, alone, cannot provide a holistic understanding of the water quality drivers of ecosystem health. That understanding served as a starting point for our gap analysis.

A knowledge and data gap analysis can propose topical areas and priority opportunities that are uniquely suited to a particular agency's mission. Here the WMA's NWQP carried out the gap analysis with an aim to serve WMA's Integrated Water Prediction (IWP) (https://www.usgs.gov/mission-areas/water-resources/science/integrated-water-prediction-iwp) and Integrated Watershed Availability Assessments (IWAAS) programs (https://www.usgs.gov/mission-areas/water-resources/science/integrated-water-availability-assessments-iwaas). Both parent programs emphasize the identification of causal factors with IWP focusing on forecasting future outcomes. Our gap analysis focused on prioritizing new capabilities beyond the current expertise of USGS in streamflow and constituent concentration trends toward developing integrated capabilities for assessment and modeling of the water-quality drivers of aquatic ecosystem health (table A1).

Many important topics for ecosystem health are not in the purview of the USGS WMA. For example, building contaminant exceedance criteria for specific organisms and life stages, although crucial for establishing contaminant exceedance criteria for ecosystems, is a task that is best suited for EPA's combined research and regulatory authority that supports specialty areas through research contracting with universities. Similarly, although pathogens rank highly as an impairment of beneficial uses of aquatic ecosystems, the USGS WMA currently has limited involvement compared to other agencies.

Table A1. Opportunities for the U.S. Geological Survey (USGS) Water Mission Area (WMA) in aquatic ecosystem health.

[WMA, USGS Water Resources Mission Area (https://www.usgs.gov/mission-areas/water-resources); NWQP, USGS WMA National Water Quality Program (https://www.usgs.gov/programs/national-water-quality-program); IWP, WMA Integrated Water Prediction (https://www.usgs.gov/mission-areas/water-resources/science/integrated-water-prediction-iwp); IWAAS, WMA Integrated Watershed Availability Assessments (https://www.usgs.gov/mission-areas/water-resources/science/integrated-water-availability-assessments-iwaas.]

What	Who	Why	Where	How
Ecosystems are vulnerable to short-term disturbances and long-term alterations that threaten ecosystem health and societal values including water purification, species diversity, high-value recreational species, safe recreational waters, and drinking water.	WMA WQP developing capabilities for IWP and IWAAS programs. Priorities reflect equally: (1) stakeholder rank of importance, (2) USGS capabilities and growth opportunities, and (3) current data availability.	New capabilities needed in data collection and analysis to advance beyond characterizing trends of single constituents in streamflow to inform predictions of eco-health. Serve timely information to support stakeholder decision making and prioritization of regulatory and management actions to counter threats.	All waters, surface and subsurface, that affect surface water availability and quality now, and for decades in the future. Assessments and models vary in spatial extent from individual watersheds to the Nation, at timescales ranging from days to decades, to inform predictions of eco-health.	Integrated assessments and models of water quality drivers of eco-health. Products may involve:(1) early warnings for recreational users, water intake operators, and other stakeholders (2) vulnerability assessments for landowners, managers, and other stakeholders

Potential Topics for an Eco-Health Gap Analysis

During discussions of potential topical areas, the ecosystem health gap analysis team for the WMA Water Quality Program discussed a broad array of potential topics. For example, the team discussed gaps in environmental toxicology that limit opportunities for managing ecosystems. To assess ecological toxicity more fully, it was argued that more process-based research is needed to improve predictions of organism bioexposure pathways through diet or direct uptake (Mebane and others, 2020). Such work can classify key bioexposure pathways to emerging contaminants of concern, and to broadly characterize uptake mechanisms for classes of contaminants at various levels of the food web. Such information can be used to refine how bioexposure and bioavailability are measured, managed, and regulated. The USGS could assist collaborators in expanding the data sources for modeling the fate of many anthropogenic and geogenic contaminants, including innovative modeling of anthropogenic contaminants. An example is advanced model tracking of wastewater inputs to downstream locations (Barber and others, 2022).

The team also discussed how historically the USGS and other agencies have typically modeled only single contaminant threats, yet the most common threats to aquatic ecosystems in the United States are attributed to the simultaneous presence and mixture of several contaminants (Masoner and others, 2019). Salinization of the Nation's freshwaters is one of the most widespread manifestations (Kaushal and others, 2018). It is a complicated problem for ecosystem health because of the broad-based "chemical cocktails" that can be involved and because of the difficulty in anticipating outcomes for aquatic communities (Dugan and others, 2017). There are differential lethal and sublethal effects of salinity on specific organisms, as well as higher level effects on community structure and function, in addition to the ancillary effects of changing salinity on mobilization of contaminants stored in sediments. All of these have potentially cascading effects on downstream ecosystems. Likewise, many EPA Superfund sites hosting a myriad of industrial contaminants are in floodplains, exacerbating the potential for rapid mobilization and spreading of contaminants to downstream areas.

There is growing recognition of the need for multi-factor controls for aquatic health involving physical, biogeochemical, and biological interactions that threaten aquatic ecosystems (Community Coordinating Group on Integrated Hydro-Terrestrial Modeling, 2020). For example, widespread deoxygenation has occurred in warming temperate rivers of the United States and Europe (Zhi and others, 2023) with steeper trends in urban and agricultural landscapes consistent with hydrologic and biogeochemical drivers (Blaszczak and others, 2022). Excessive algal growth can arise from the coupled influences of higher nutrient inputs, moderate to high light availability, and extended water residence times in rivers regulated for navigation in the intensively farmed Midwestern United States (Giblin and others, 2022). Excess nutrients and organic carbon (OC) may derive from watershed activities such as agriculture and rangeland management, urbanization, and stormwater management, as well as wildfire, forest roads and related forest management practices (Bernhardt and others, 2022). Excess nutrients and OC also may be derived from within the river network, for example, from mobilization from reservoir or stormwater pond sediments (Taguchi and others, 2020) or from release from storage in living algal biomass or from storage in river pools or riparian zones. Dams not only alter the flow regime but also play a role by storing nutrients and fine particulate organic matter that may later be released to fuel excessive algal blooms (Wang and others, 2019).

In addition, excessive algal blooms can overload aquatic systems with labile organic matter that buries coarse-grained biological habitat with fine sediment, and consumes oxygen, sometimes leading to hypoxia and fish kills.

The result of anthropogenic alterations has been eutrophication of surface waters—major shifts in metabolism and trophic dynamics that alter aquatic food webs in rivers and their downstream receiving waters including lakes, reservoirs, and estuaries (Dodds and Smith, 2016). Larger and longer lasting algal blooms can lead to more frequent recreational area closures, fouled water treatment operations, and releases of biological toxins that threaten wildlife, pets, and humans (Glibert, 2017).

Eutrophication of surface waters accounts for the highest number of reported impairments by EPA. Eutrophication is not often reported directly. Instead, eutrophication is often reported in terms of the expected drivers or associated water-quality changes, such as excessive nutrients (ranked number 2 in terms of the number of reported impairments) and oxygen depletion by organic enrichment (ranked number 4) (EPA, 2017). Those broad water-quality impairments are often accompanied by related broad-based water-quality impairments such as salinity (ranked number 12). Notable exceptions to those broad-based water-quality impairments are specific anthropogenic and bio- or geogenic contaminants, such as pathogens (ranked number 1); trace metals, such as arsenic (As), copper (Cu), and selenium (Se) (ranked number 3); and mercury (Hg) which ranked number 7 among all reported impairments (EPA, 2017).

Other highly ranked impairments in the Nation that relate to eutrophication and to habitat suitability for high-value aquatic species include high total suspended solids (ranked number 6) and high temperature (ranked number 10). Fine grained sediment (less than 0.063 millimeter [mm]) is a key impairment of United States waterways that reduces water clarity, clogs bed sediments, raises temperature, and increases biological oxygen demand that can suffocate fauna and fish eggs (Cluer and Thorne, 2014). Also, longer and hotter fire seasons in the western United States are increasing the loading of fine sediment with a high black carbon content to rivers (Wagner and others, 2015) which stresses stream ecosystems by increasing turbidity and biological oxygen demand. In addition, increased sedimentation in western rivers may exacerbate channel aggradation and flooding (Wagner and others, 2015). In the Northeastern United States, where a wetter and warmer climate is predicted, an important question is whether increased loadings of sediment-associated nutrients (Noe and others, 2020) will exacerbate algal blooms and hypoxic events.

Nutrient and fine sediment contamination and harmful algal blooms (HABs), acting together, can substantially affect local economies throughout the Nation. For that reason, hypoxia and HABs were identified by a recent workshop of seven Federal agencies and many universities addressing the need for integrated hydro-terrestrial modeling to serve stakeholders (Community Coordinating Group on Integrated Hydro-Terrestrial Modeling, 2020). Alongside floods and western water, hypoxia and HABs were proposed as one of three grand challenges by the Community Coordinating Group on Integrated Hydro-Terrestrial Modeling (2020). Integrated hydro-terrestrial modeling of coupled constituents could support development of early warning capabilities for excessive algal blooms and hypoxia.

Selected Topical Areas for the Gap Analysis

Team deliberations during the fall of 2020 identified four key topical areas for an in-depth gap analysis. Team selections were vetted in discussions and presentations with a wider set of USGS colleagues. Many potential topics were discussed that could play an important role in improving USGS service to stakeholders who need the information to assess potential effectiveness of management strategies to protect ecosystem services and water supply.

The following four key topical areas were selected for an in-depth gap analysis of water-quality drivers of aquatic ecosystem health:

1. Coupled nutrient-carbon cycle processes and related ecological-flow drivers,
2. Anthropogenic and geogenic toxin bioexposure,
3. Fine sediment drivers, and
4. Freshwater salinization.

The eco-health gap analysis that follows assesses for each of the selected topics the (1) status of knowledge and key limitations, (2) identification of specific gaps, (3) approaches to address gaps, (4) prioritization of gaps with timelines, and (5) potential outcomes for water-quality stakeholders. Topics included a discussion of the role of data collection, issues of scale and transferability, and appropriate analysis approaches to address stakeholder needs for scientific information about water-quality and ecological-flow-regime (“eco-flow”) drivers of aquatic ecosystem health (Suen and Eheart, 2006). As the science and stakeholder needs evolve, there is need for program evolution to keep pace—hence this gap analysis with proposed approaches for moving forward in addressing issues today as well as emerging issues for future aquatic ecosystem health.

References Cited

Baldaccini, G.N., Leone, L.M. and Taddei, C., 2009. The running waters macroinvertebrates community—Sampling techniques. Journal of Environmental Monitoring, v. 11, no. 4, p. 756–760, https://doi.org/10.1039/B818280A.

Barber, L.B., Faunce, K.E., Bertolatus, D.W., Hladik, M.L., Jasmann, J.R., Keefe, S.H., Kolpin, D.W., Meyer, M.T., Rapp, J.L., Roth, D.A., and Vajda, A.M., 2022, Watershed-scale risk to aquatic organisms from complex chemical mixtures in the Shenandoah River: Environmental Science and Technology, v. 56, no. 2, p. 845–861, https://doi.org/10.1021/acs.est.1c04045.

Barnes, K.K., Kolpin, D.W., Furlong, E.T., Zaugg, S.D., Meyer, M.T., and Barber, L.B., 2008, A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States—I) Groundwater: Science of the Total Environment, v. 402, nos. 2–3, p. 192–200, https://doi.org/10.1016/j.scitotenv.2008.04.028.

Bernhardt, E.S., Savoy, P., Vlah, M.J., Appling, A.P., Koenig, L.E., Hall Jr, R.O., Arroita, M., Blaszczak, J.R., Carter, A.M., Cohen, M. Harvey, J.W., Heffernan, J.B., Helton, A.M., Hosen, J.D., Kirk, L., McDowell, W.H., Stanley, E.H., Yackulic, C.B., and Grimm, N.B., 2022, Light and flow regimes regulate the metabolism of rivers: Proceedings of the National Academy of Sciences, v. 119, no. 8, 5 p., https://doi.org/10.1073/pnas.2121976119.

Blaszczak, J.R., Koenig, L.E., Mejia, F.H., Gómez-Gener, L., Dutton, C.L., Carter, A.M., Grimm, N.B., Harvey, J.W., Helton, A.M. and Cohen, M.J., 2022, Extent, patterns, and drivers of hypoxia in the world's streams and rivers: Limnology Oceanography Letters, https://doi.org/10.1002/lol2.10297.

Bradley, P.M., Journey, C.A., Button, D.T., Carlisle, D.M., Clark, J.M., Mahler, B.J., Nakagaki, N., Qi, S.L., Waite, I.R., and Van Metre, P.C., 2016, Metformin and other pharmaceuticals widespread in wadeable streams of the southeastern United States: Environmental Science & Technology Letters, v. 3, no. 6, p. 243–249, https://doi.org/10.1021/acs.estlett.6b00170.

Brauman, K.A., Daily, G.C., Duarte, T.K.E. and Mooney, H.A., 2007, The nature and value of ecosystem services—An overview highlighting hydrologic services: Annual Review of Environment and Resources, v. 32, p. 67–98, https://doi.org/10.1146/annurev.energy.32.031306.102758.

Briggs, M.A., Harvey, J.W., Hurley, S.T., Rosenberry, D.O., McCobb, T., Werkema, D., and Lane, J.W., Jr., 2018, Hydrogeologic controls on preferential brook trout spawning habitat in a coastal stream: Hydrology and Earth System Sciences, v. 22. no. 12, https://doi.org/10.5194/hess-2017-693.

Burford, M.A., Carey, C.C., Hamilton, D.P., Huisman, J., Paerl, H.W., Wood, S.A., and Wulff, A., 2020, Perspective—Advancing the research agenda for improving understanding of cyanobacteria in a future of global change: Harmful Algae, v. 91, article 101601, https://doi.org/10.1016/j.hal.2019.04.004.

Canadell, J.G., Le Quéré, C., Raupach, M.R., Field, C.B., Buitenhuis, E.T., Ciais, P., Conway, T.J., Gillett, N.P., Houghton, R.A., and Marland, G., 2007, Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks: Proceedings of the National Academy of Sciences, v. 104, no. 47, p. 18866–18870, https://doi.org/10.1073/pnas.0702737104.

Carlisle, D., Meador, M.R., Short, T.M., Tate, C.M., Gurtz, M.E., Bryant, W.L., Falcone, J.A., and Woodside, M.D., 2013, The quality of our Nation's waters—Ecological health in the Nation's streams, 1993–2005: U.S. Geological Survey Circular 1391, 120 p., https://doi.org/10.3133/cir1391.

Chapman, P.M., Adams, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P., eds., 2010, Ecological Assessment of selenium in the aquatic environment: CRC Press, 358 p.

Cluer, B. and Thorne, C., 2014, A stream evolution model integrating habitat and ecosystem benefits: River Research and Applications, v. 30, no. 2, p. 135–154, https://doi.org/10.1002/rra.2631.

Community Coordinating Group on Integrated Hydro-Terrestrial Modeling, 2020, Integrated Hydro-terrestrial modeling—Development of a National Capability, *in* Report of an Interagency workshop, September 4–6, 2019: National Science Foundation, U.S. Department of Energy, and U.S. Geological Survey, 180 p., https://doi.org/10.25584/09102020/1659275.

Dodds, W.K., and Smith, V.H., 2016, Nitrogen, phosphorus, and eutrophication in streams: Inland Waters, v. 6, no. 2, p. 155–164, https://doi.org/10.5268/IW-6.2.909.

Dugan, H.A., Bartlett, S.L., Burke, S.M., Doubek, J.P., Krivak-Tetley, F.E., Skaff, N.K., Summers, J.C., Farrell, K.J., McCullough, I.M., Morales-Williams, A.M., Roberts, D.C., Ouyang, Z., Scordo, F., Hanson, P.C., and Weathers, K.C., 2017, Salting our freshwater lakes: Proceedings of the National Academy of Sciences, v. 114, no. 17, p. 4453–4458, https://doi.org/10.1073/pnas.1620211114.

Durbecq, A., Jaunatre, R., Buisson, E., Cluchier, A. and Bischoff, A., 2020, Identifying reference communities in ecological restoration—The use of environmental conditions driving vegetation composition: Restoration Ecology, v. 28, no. 6, p. 1445–1453, https://doi.org/10.1111/rec.13232.

Finzi, A.C., Austin, A.T., Cleland, E.E., Frey, S.D., Houlton, B.Z., and Wallenstein, M.D., 2011, Responses and feedbacks of coupled biogeochemical cycles to climate change: examples from terrestrial ecosystems: Frontiers in Ecology and the Environment, v. 9, no. 1, p. 61–67, https://doi.org/10.1890/100001.

Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Barber, L.B., and Thurman, M.E., 2008, A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States—II) Untreated drinking water sources: Science of the Total Environment, v. 402, nos. 2–3, p. 201–216, https://doi.org/10.1016/j.scitotenv.2008.02.021.

Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., and Sutton, M.A., 2008, Transformation of the nitrogen cycle—Recent trends, questions, and potential solutions: Science, v. 320, no. 5878, p. 889–892, https://doi.org/10.1126/science.1136674.

Giblin, S.M., Larson, J.H., and King, J.D., 2022, Environmental drivers of cyanobacterial abundance and cyanotoxin production in backwaters of the Upper Mississippi River: River Research and Applications, v. 38, no. 6, p. 1115–1128, https://doi.org/10.1002/rra.3987.

Gilbert, N., 2009, Environment—The disappearing nutrient: Nature, v. 461, no. 7265, p. 716–718, https://doi.org/10.1038/461716a.

Gilliam, J.W., 1994, Riparian wetlands and water quality: Journal of environmental quality, v. 23, no. 5, p. 896–900, https://doi.org/10.2134/jeq1994.00472425002300050007x.

Glibert, P.M., 2017, Eutrophication, harmful algae and biodiversity—Challenging paradigms in a world of complex nutrient changes: Marine Pollution Bulletin, v. 124, no. 2, p. 591–606, https://doi.org/10.1016/j.marpolbul.2017.04.027.

Glibert, P. M., Allen, J.I., Bouwman, A.F., Brown, C.W., Flynn, K.J., Lewitus, A.J., and Madden, C.J., 2010, Modeling of HABs and eutrophication—Status, advances, challenges: Journal of Marine Systems, v. 83, nos. 3–4, p. 262–275, https://doi.org/10.1016/j.jmarsys.2010.05.004.

Golden, H.E., and Hoghooghi, N., 2018, Green infrastructure and its catchment-scale effects—An emerging science: WIREs Water, v. 5, no. 1, article e1254, 14 p., https://doi.org/10.1002/wat2.1254.

Harvey, J., Gomez-Velez, J., Schmadel, N., Scott, D., Boyer, E., Alexander, R., Eng, K., Golden, H., Kettner, A., Konrad, C., Moore, R., Pizzuto, J., Schwarz, G., Soulsby, C., and Choi, J., 2019, How hydrologic connectivity regulates water quality in river corridors: Journal of the American Water Resources Association, v. 55, no. 2, p. 369–381, https://doi.org/10.1111/1752-1688.12691.

Kaushal, S.S., Likens, G.E., Pace, M.L., Utz, R.M., Haq, S., Gorman, J., and Grese, M., 2018, Freshwater salinization syndrome on a continental scale: Proceedings of the National Academy of Sciences, v. 115, no. 4, p. E574–E583, https://doi.org/10.1073/pnas.1711234115.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., and Buxton, H.T., 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000—A National Reconnaissance: Environmental Science & Technology, v. 36, no. 6, p. 1202–1211, https://doi.org/10.1021/es011055j.

Lynch, L.M., Sutfin, N.A., Fegel, T.S., Boot, C.M., Covino, T.P. and Wallenstein, M.D., 2019, River channel connectivity shifts metabolite composition and dissolved organic matter chemistry: Nature Communications, v. 10, no. 1, article 459, 11 p., https://doi.org/10.1038/s41467-019-08406-8.

Masoner, J.R., Kolpin, D.W., Cozzarelli, I.M., Barber, L.B., Burden, D.S., Foreman, W.T., Forshay, K.J., Furlong, E.T., Groves, J.F., Hladik, M.L., Hopton, M.E., Jaeschke, J.B., Keefe, S.H., Krabbenhoft, D.P., Lowrance, R., Romanok, K.M., Rus, D.L., Selbig, W.R., Williams, B.H., and Bradley, P.M., 2019, Urban stormwater—An overlooked pathway of extensive mixed contaminants to surface and groundwaters in the United States: Environmental Science & Technology, v. 53, no. 17, p. 10070–10081, https://doi.org/10.1021/acs.est.9b02867.

Mebane, C.A., Chowdhury, M.J., De Schamphelaere, K.A.C., Lofts, S., Paquin, P.R., Santore, R.C., and Wood, C.M., 2020, Metal bioavailability models—Current status, lessons learned, considerations for regulatory use, and the path forward: Environmental Toxicology and Chemistry, v. 39, no. 1, p. 60–84, https://doi.org/10.1002/etc.4560.

Noe, G.B., Cashman, M.J., Skalak, K., Gellis, A., Hopkins, K.G., Moyer, D., Webber, J., Benthem, A., Maloney, K., Brakebill, J., Sekellick, A., Langland, M., Zhang, Q., Shenk, G., Keisman, J., and Hupp, C., 2020, Sediment dynamics and implications for management—State of the science from long-term research in the Chesapeake Bay watershed, USA: WIREs Water, v. 7, no. 4, article e1454, 28 p., https://doi.org/10.1002/wat2.1454.

Poff, N.L., Allan, J.D., Bain, M.B., Karr, J.R., Prestegaard, K.L., Richter, B.D., Sparks, R.E., and Stromberg, J.C., 1997, The natural flow regime: BioScience, v. 47, no. 11, p. 769–784, https://doi.org/10.2307/1313099.

Poff, N.L., Richter, B.D., Arthington, A.H., Bunn, S.E., Naiman, R.J., Kendy, E., Acreman, M., Apse, C., Bledsoe, B.P., Freeman, M.C., Henriksen, J., Jacobson, R.B., Kennen, J.G., Merritt, D.M., O'Keeffe, J.H., Olden, J.D., Rogers, K., Tharme, R.E., and Warner, A., 2010, The ecological limits of hydrologic alteration (ELOHA)—A new framework for developing regional environmental flow standards: Freshwater Biology, v. 55, no. 1, p. 147–170, https://doi.org/10.1111/j.1365-2427.2009.02204.x.

Suen, J.P. and Eheart, J.W., 2006, Reservoir management to balance ecosystem and human needs—Incorporating the paradigm of the ecological flow regime: Water Resources Research, v. 42, no. 3, https://doi.org/10.1029/2005WR004314.

Taguchi, V.J., Olsen, T.A., Natarajan, P., Janke, B.D., Gulliver, J.S., Finlay, J.C., and Stefan, H.G., 2020, Internal loading in stormwater ponds as a phosphorus source to downstream waters: Limnology and Oceanography Letters, v. 5, no. 4, p. 322–330, https://doi.org/10.1002/lol2.10155.

U.S. Environmental Protection Agency [EPA], 2017, National Summary of State Information: U.S. Environmental Protection Agency, accessed January 2021, at https://iaspub.epa.gov/waters10/attains_nation_cy.control. [Also available at https://www.epa.gov/waterdata/attains]

U.S. Environmental Protection Agency [EPA], 2020a, National rivers and streams assessment 2013–2014—A collaborative survey, NRSA dashboard: U.S. Environmental Protection Agency, National Rivers and Streams Assessment (NRSA), NRSA data dashboard website, accessed January 5, 2021, at https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=OWOW&dirEntryID=342812.

U.S. Environmental Protection Agency [EPA], 2020b, National rivers and streams assessment 2013–2014—A collaborative survey: U.S. Environmental Protection Agency, EPA 841-R-19-001, 65 p., accessed January 5, 2021, at https://www.epa.gov/system/files/documents/2021-10/nrsa_13-14_report_508_ci_2021-10-15.pdf.

Wagner, S., Cawley, K.M., Rosario-Ortiz, F.L. and Jaffé, R., 2015, In-stream sources and links between particulate and dissolved black carbon following a wildfire: Biogeochemistry, v. 124, p.145–161, https://doi.org/10.1007/s10533-015-0088-1.

Wang, Y., Hu, Y., Yang, C., Wang, Q., and Jiang, D., 2019, Variations of DOM quantity and compositions along WWTPs-river-lake continuum—Implications for watershed environmental management: Chemosphere, v. 218, p. 468–476, https://doi.org/10.1016/j.chemosphere.2018.11.037.

Wohl, E., Bledsoe, B.P., Jacobson, R.B., Poff, N.L., Rathburn, S.L., Walters, D.M. and Wilcox, A.C., 2015, The natural sediment regime in rivers—Broadening the foundation for ecosystem management: BioScience, v. 65 no. 4, p. 358–371, https://doi.org/10.1093/biosci/biv002.

Wymore, A.S., Ward, A.S., Wohl, E., and Harvey, J.W., 2023, Viewing River Corridors through the Lens of Critical Zone Science: Frontiers in Water, v. 5, https://doi:0.3389/frwa.2023.1147561.

Zhi, W., Klingler, C., Liu, J., and Li, L., 2023, Widespread deoxygenation in warming rivers: Nature Climate Change, v. 13, p. 1105–1113, https://doi.org/10.1038/s41558-023-01793-3.

Knowledge Gaps and Opportunities in Water-Quality Drivers of Aquatic Ecosystem Health
Edited by Judson W. Harvey, Christopher H. Conaway, Mark M. Dornblaser, Allen C. Gellis, A. Robin Stewart, and Christopher T. Green
[Also see https://doi.org/10.3133/ofr20231085]

Chapter B

Coupled Nutrient-Carbon Cycle Processes and Related Ecological-Flow Drivers of Aquatic Health

By Mark M. Dornblaser, Kimberly P. Wickland, Deborah A. Repert, Richard L. Smith, and Judson W. Harvey

Purpose and Scope

This chapter addresses knowledge gaps that, if filled, could improve predictions of aquatic ecosystem health as affected by coupled nutrient-carbon cycle processes and related ecological flow drivers. The gaps identified in this chapter are not intended to be comprehensive but are instead focused on key opportunities for the U.S. Geological Survey (USGS) Water Resources Mission Area (WMA, https://www.usgs.gov/mission-areas/water-resources). Nutrient effects on beneficial uses of water are not addressed in this chapter but are covered in Chapter E of Tesoriero and others (2024), "Improving Predictions of Nitrogen Effects on Beneficial Uses of Water," the companion Open-File Report to this publication.

Statement of the Problem

The biogeochemical cycles of carbon (C), nitrogen (N), and phosphorus (P) are fundamental to life, and they are coupled to one another through basic stoichiometry requirements of organisms and oxidation-reduction reactions of metabolism (Sterner and Elser, 2002; Schlesinger and others, 2011). Human activities have radically changed the amount and distribution of these elements; for example, atmospheric carbon dioxide (CO_2) concentrations have increased by 40 percent or more since the beginning of the Industrial Revolution (Canadell and others, 2007), reactive N in the biosphere has doubled since 1950 (Galloway and others, 2008), and mining of P for fertilizers has redistributed it across the Earth (Gilbert, 2009). These individual and collective changes in C, N, and P are leading to the reorganizing of biological communities in terrestrial and aquatic systems, with important implications for ecosystem health (Finzi and others, 2011). This chapter summarizes gaps in our understanding of coupled nutrient-carbon cycle processes and related ecological flow regime ("eco-flow") drivers (Suen and Eheart, 2006) and proposes a series of approaches across multiple scales (microbial-to-river reach) which will address these gaps, providing data and understanding that could aid ecosystem-health modeling efforts.

On an annual basis the U.S. Environmental Protection Agency (EPA) ranks by number the stakeholder-reported impairments of aquatic health and beneficial use of surface waters across the Nation (EPA, 2017). Impairments associated with eutrophication of surface waters rank among the highest priorities, with excessive nutrients ranked number 2, low dissolved oxygen ranked number 4, high total suspended solids ranked number 6, and high temperatures ranked number 10 (EPA, 2017). Despite efforts to reduce nutrient inputs to waterways, land use and climate change have resulted in trends that are generally not improving. The EPA found 43 percent of national rivers and streams were of poor quality according to a rating based on total nitrogen (TN) with no change from 2008–2009 to 2013–2014; for total phosphorus (TP), they found that 58 percent of rivers and streams had poor quality in 2013–2014, up from 47 percent in 2008–2009 (EPA, 2017). U.S. Geological Survey (USGS) trend analysis for the years 1992–2012 showed that while nitrate (NO_3), TP, ammonium (NH_4), soluble reactive P (SRP), and TN were decreasing at a majority of urban sites, there was a lack of nutrient reduction at agricultural sites (Stets and others, 2020). An important question remains as to whether nutrient reduction efforts at agricultural sites have not been large enough, or whether legacy nutrients are causing a lag in river response to those efforts (Stackpoole and others, 2019).

Eutrophication and other issues concerning surface-water quality are often assessed in the context of a single constituent; for example, TN or TP commonly is targeted for total maximum daily load (TMDL) regulation to address impaired waters, whereas other factors such as temperature, dissolved oxygen (O), fine sediment, dissolved and particulate organic carbon (DOC, POC), and antibiotics are not addressed. Also not addressed are the complex interactions among multiple biogeochemical processes and flow-related physical drivers (for example, water residence time, mixing and stratification, and oxygen reaeration) that influence the onset, severity, duration, and frequency of eutrophication events. A broad array of biologically mediated N cycle processes (including nitrification, denitrification, and microbial respiration), along with organic carbon (OC) reactions, strongly influence the ecological health of aquatic systems. These coupled or linked physical and biological reaction processes and their effects on the fate of constituents and on ecological health rarely are considered in regulatory measures to protect ecosystem health. Nevertheless, the coupled cycling of constituents and their interactions with physical mixing and gas exchange is foundational to water quality and ecosystem health (see fig. B1).

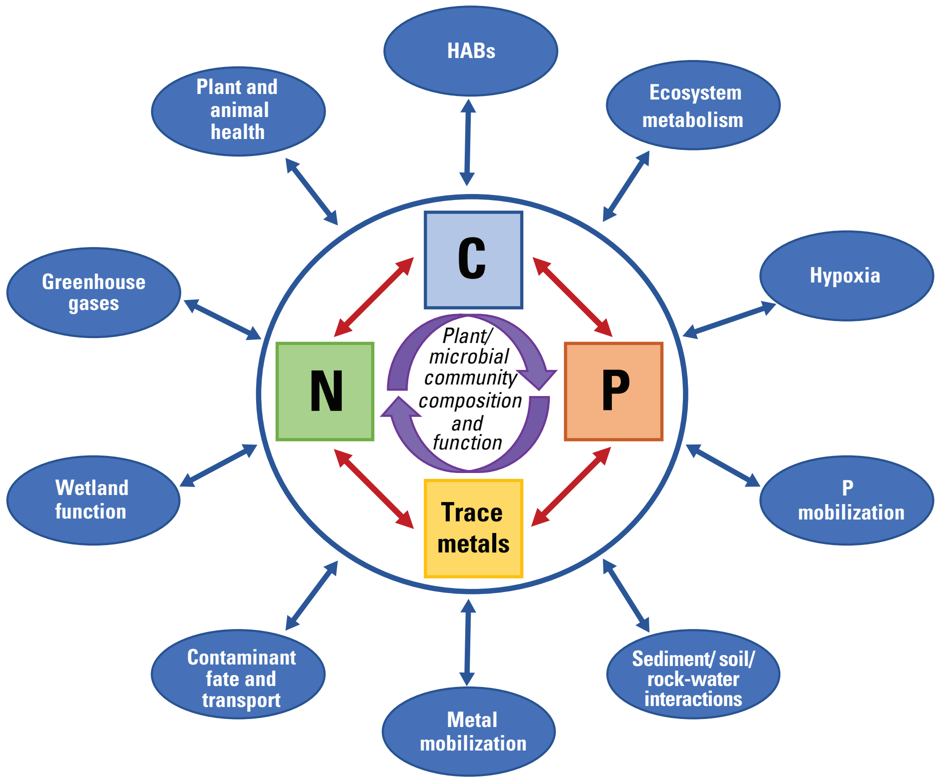


Figure B1. Diagram of coupled nutrient-carbon processes and their effect on aquatic eco-health. Inner circle coupled interactions (red arrows) have substantial consequences and feedback on key ecosystem functions and characteristics (blue arrows). Modified from Finzi and others (2011). C, carbon; N, nitrogen; P, phosphorus; HABs, harmful algal blooms.

An example of a coupled reaction is the linked mineralization reactions of an organic contaminant, which often result in the production of a related degradate compound, rather than complete disappearance of the parent compound. Coupled redox reactions can affect contaminant degradation, sequestration, and transport. For example, iron (Fe) oxidation coupled to nitrate reduction produces Fe oxides that sequester arsenic (As) and P. Sulfate reduction rates are a key consideration in modeling of mercury (Hg) cycling in streambeds (Marvin-DiPasquale and others, 2009). Another example is nutrient redox reactions that potentially affect reaction pathways and the form of gaseous end-products, such as nitrous oxide (N_2O), that affect greenhouse gas emissions, or the redox state of Fe that may lead to P sequestration by attachment to sediments under oxic conditions or release under anoxic conditions that can fuel harmful algal blooms (HABs). Process interactions can be either synergistic or antagonistic, resulting in positive or negative effects. For example, antibiotic inhibition of microbial processes in watersheds can inhibit or delay biogeochemical processes considered relevant to ecosystem health and can couple with hydraulic transport to downstream reaches, where subsequent processes may differ from upstream processes. Coupled constituents and processes are relevant to all stakeholders concerned with ecosystem health and can be considered essential for modeling the overall effect of water quality and contaminants on ecosystems and for addressing impairment of aquatic ecological health (Finzi and others, 2011; Bruggeman and Bolding, 2014).

Status of Knowledge and Key Limitations

A summary of C-N-P constituents, their relevance to aquatic ecosystem health, and stakeholder level of concern is provided in table B1. The table provides information about primary constituents of concern, connections to potential aquatic and human impairments, and EPA rankings under nationwide Clean Water Act of 1972, in section 303(d) (CWA; 33 U.S.C. 1251 et seq.; https://www.epa.gov/tmdl) listings (EPA, 2017).

There has been substantial progress in characterizing sources and predicting the movement and attenuation of key constituents, particularly N, across the landscape and through surface water networks (National Research Council, 2002; Schmadel and others, 2019). Ecosystem syndromes such as excessive algal growth, high turbidity, hypoxia, and HABs often result from the combined effects of excess N, P, and OC coupled with high temperature and long residence times

Table B1. Summary of nutrient-carbon constituents, relevance to aquatic ecosystem health, and previous findings from the U.S. Environmental Protection Agency rankings (2017).

[DOC, dissolved organic carbon; TOC, total organic carbon; O, oxygen, Cl, chlorine; EPA, U.S. Environmental Protection Agency; HABs, harmful algal blooms; 303(d), Clean Water Act Section 303(d); TDN, total dissolved nitrogen; TN, total nitrogen; %, percent; NH_4, ammonium; N, nitrogen; NH_3, ammonia; mg/L, milligrams per liter; NO_3, nitrate; Fe, iron; P, phosphorus; TP, total phosphorus; TDP, total dissolved phosphorus or orthophosphate.]

Constituent	Relevance to aquatic ecosystem health	Previous findings[1]
DOC, TOC: including particulate organic carbon derived from in-stream and terrestrial sources strongly influenced by flow, agriculture, and urbanization; often stormflow generated from soils, wetlands, ponds, and reservoirs.	Fuels bacterial respiration which consumes O and may contribute to hypoxia; may affect nutrient availability for algae growth; binds with metals; reacts with Cl to form carcinogenic disinfection byproducts.	EPA does not specifically rank these constituents, but implicitly DOC and TOC are linked to nutrient, O, and eutrophication concerns.
Nutrients: fertilized agricultural and suburban areas, livestock pens and waste ponds, wastewater treatment plants, sewer, and septic.	Can lead to HABs, hypoxia/anoxia.	EPA-303(d): Ranks 2nd in national ranking of reported impairments; Ranks 6th as a "top 5" concern in 19% of large river basins.
TDN/TN: includes sources above as well as atmospheric deposition.	Can lead to HABs, hypoxia/anoxia.	EPA found 43% of national stream miles were of poor quality for TN in 2013–2014 and no change over 2008–2009.
NH_4: fertilizers, decomposition of organic matter, gas exchange, animal and human waste, N fixation, municipal effluent, atmospheric N deposition.	Toxic buildup in tissues and blood; pH and temperature can affect toxicity; can lead to HABs.	EPA: NH_3 can be toxic to aquatic plants, invertebrates, and fish at concentrations less than 1 mg/L.
NO_3: fertilizers, animal and human waste, municipal effluent, atmospheric N deposition.	In drinking water—in the body, nitrate reduced to nitrite which reacts with Fe in hemoglobin causing methemoglobinemia (blue baby syndrome); can also lead to HABs.	EPA: NO_3, in conjunction with P, accelerates eutrophication; can lead to changes in aquatic species composition.
TP, TDP: Wastewater treatment; fertilizer; septic systems; animal manure runoff; also includes geogenic sources.	Can lead to HABs, increased biological O demand.	EPA found 58% of national stream miles were of poor quality for TP in 2013–2014, up from 47% in 2008–2009.

[1]Information from EPA, 2017.

(Community Coordinating Group on Integrated Hydro-Terrestrial Modeling, 2020). Identifying and separating the role of contemporary and legacy sources of nutrients is a key concern. Distinguishing these sources requires understanding of complex hydrogeochemical interactions. For example, legacy P export depends on a soil's mineral composition, organic matter content, and redox conditions (Stackpoole and others, 2019). Out-of-balance behaviors such as HABs suffocate aquatic communities, threaten water supplies and increase treatment costs, endanger recreation, lower property values, and pose long term challenges to biologically diverse and sustainable water resources. The USGS and other Federal agencies are only beginning to formulate an effective strategy for improving nationwide capabilities for predicting excess nutrients, hypoxia, and HABs (Community Coordinating Group on Integrated Hydro-Terrestrial Modeling, 2020).

A lack of understanding of coupled processes has resulted in substantial limitations for predicting and managing aquatic ecological health. For example, coupled nutrient-C reactions, ancillary physicochemical drivers such as temperature, redox, and pH, or coupling between physical processes such as residence time and reaeration of water bodies may have dominant outcomes for ecological health. "One of the most challenging steps in the development of coupled hydrodynamic-biogeochemical models is the combination of multiple, often incompatible computer codes that describe individual physical, chemical, biological and geological processes" (Bruggeman and Bolding, 2004, p 249). Often there is a failure to recognize that N in the environment does not solely function as a nutrient as in the case where it is an electron acceptor in redox reactions. While individual N and P cycle processes are important, there are also abundant interactions with constituents that control their fate and transport throughout the hydrosphere by affecting N and P speciation and physical state. These processes often are coupled to the fate and transport of water quality constituents such as DOC and POC (Strauss and Lamberti, 2000). Stoichiometric relationships in biological uptake may drive proportional removal of N and P from flowing waters that lead to nutrient limitations for particular biological communities (Glibert, 2017). Furthermore, Fe and Mn precipitates on sediment that sequester or mobilize particular forms of N and P, subject to redox or pH conditions (Taguchi and others, 2020).

Microorganisms are coupled to numerous biogeochemical cycles in the environment (Falk and others, 2019) and microbial functional diversity is recognized among microbial ecologists as an essential link between biodiversity patterns and ecosystem functioning (Escalas and others, 2019). However, despite the fact that biogeochemical cycles have coevolved and often directly affect the outcome of one another, these cycles and the associated microbial communities are often studied in isolation (Falkowski and others, 2008). Excessive nutrient and contaminant inputs to ground and surface waters from urban and agricultural land use activity can have dramatic effects on the microbial community composition and function and ultimately on water quality processes and ecosystem health. Microorganisms can serve as buffers against certain legacy pollutants or as bioindicators of stressed ecosystems. While the microbial community can adapt by using gene transfer mechanisms and functional redundancy, taxonomic and functional diversity indices can be used to assess increased or decreased stressors to a particular environment. “Investigations into active transcripts associated with nitrogen metabolism are key to understanding site-specific nutrient dynamics and ecosystem health” (Weisener and others, 2017, p. 702). By understanding how the microbial community responds to environmental stressors, researchers and managers can better predict how a particular environment will be able to respond to physical-chemical-biological drivers such as excess nutrients, chemical contaminants (for example, PFAS [per- and polyfluoroalkyl substances], antibiotics, nitrapyrin), and pathogens (Graham and others, 2016; Woodward and others, 2021).

Priority Knowledge Gaps in Coupled Nutrient-Carbon Processes Affecting Ecological Health

The USGS identified three main gap categories within this key topic. Detailed descriptions of each gap are presented in the following sections:

5. Multi-factor N, P, and labile C sources interacting with eco-flow drivers,
6. Redox processes controlling storage, processing, and release of N, P, Fe, As, and other contaminants,
7. Interaction between nutrient cycles and contaminants of emerging concern (CECs).

A summary of gaps, approaches, and expected outcomes is in table B2.

Gap 1. Multi-factor Nitrogen, Phosphorus, and Labile Carbon Sources Interacting with Eco-Flow Drivers

Key limitations in our understanding of coupled nutrient-carbon cycle processes include multi-factor N, P, and labile C sources and interactions with eco-flow drivers (includes river water residence time; reservoir storage; reaeration; water column light availability; associated thresholds controlling onset, severity, and duration of HABs and hypoxia/eutrophication and other adverse effects for ecosystems).

Spatial and Temporal Distributions of Labile Organic C Sources and Their Role in Coupled C-N-P Metabolic Reactions

Dissolved and particulate organic carbon (DOC, POC) are complex collections of thousands of different compounds with distinct chemical properties and turnover times that vary from minutes to millennia (Abbott and others, 2016). They provide a primary food source for food webs and can be highly reactive (“labile”). DOC and POC enter aquatic systems from the surrounding landscape with runoff and groundwater flows and are internally produced through in situ processes. Labile portions of OC are rapidly metabolized and assimilated as biomass or respired as CO_2 or methane (CH_4), while less labile OC persists and may accumulate or be transported to downstream environments. Metabolism of OC is tightly coupled with transformations in the N cycle, including denitrification (nitrate reduction to N_2) (Seitzinger, 1988; McClain and others, 2003), ammonification (Schlesinger, 1997), and nitrification (oxidation of ammonium [NH_4] to nitrate [NO_3^-]) (Strauss and Lamberti, 2000, 2002). The availability of labile (aka “biodegradable”) OC at any given place or time has important implications not only for C dynamics but also for N dynamics of aquatic ecosystems (for example, Wickland and others, 2012). For example, the presence of relatively high concentrations of labile or biodegradable DOC (BDOC) can lead to anoxia and nitrate reduction to ammonium (dissimilatory nitrate reduction, DNRA). Intermediate concentrations of BDOC often result in anoxia to suboxia and nitrate reduction to N gas (denitrification), while relatively low concentrations of BDOC will usually only couple to O consumption (aerobic respiration). The latter case will only consume nitrate in an assimilatory capacity. Conditions can exist in which mixed couples occur together in competition with each other, such as DNRA and denitrification. Simply quantifying DOC concentrations alone will not resolve the relative biodegradability of the DOC or the extent to which the DOC-nitrate reduction couple (that is, the potential for nitrate removal) could be occurring. Coupling between C and P cycling in freshwater systems is relatively less understood. However, there is evidence of close coupling of these cycles in freshwater aquatic microbial communities where labile soluble organic C enrichment can enhance microbial alkaline phosphatase production and thus increase P remineralization by organo-phosphate hydrolysis (Anderson, 2018). A comprehensive assessment of labile OC sources and degradation rates in aquatic systems, and spatial and temporal variabilities in systems of interest is necessary to accurately model coupled metabolic reactions and nutrient dynamics.

Relation Between Watershed Carbon, Nitrogen, and Phosphorus Biogeochemical Processes and Development of Harmful Algal Blooms

Nutrient concentrations and speciation are considered to be key components in the development of HABs (Gardner and others, 2017). The relations between N speciation, N:P ratios, and algal blooms are poorly understood, however. Nitrogen cycle processes can control N speciation in sediments (Li and others, 2019), across the groundwater-surface water interface (Harvey and others, 2013; Smith and others, 2019), in suspended sediment (Xia and others, 2017), and alter diel N oxidation-reduction processes in lake water (Chen and others, 2021). These processes can also affect P transport, as denitrifying bacteria can sequester P intracellularly (Zaman and others, 2021) and potentially translocate P downstream to receiving lakes and reservoirs. Most water quality studies document total P, but much less is known regarding partitioning between aqueous and sorbed P and between organic and inorganic P. The dynamic nature of N:P ratios can alter the biodiversity of the microbial community, growth rates and trophic interactions. Yet, an understanding of which forms of N and P have the greater effect (as well as when and where) remains elusive. More research could incorporate nutrient inhibition, external stresses (light, temperature), and the resultant physiological response (Glibert, 2017). Furthermore, the development of hypoxia is related to high O_2 consumption during decomposition of OC from high algal production and leads to more acidic waters from the very high levels of CO_2 that are produced (Howarth and others, 2011). Perturbations to the carbonate cycle have been shown to affect the health of aquatic organisms particularly in estuarine systems (Green and others, 2009), but the full effects are not well known. Detailed understanding of N, P, and C sources, speciation, and processes in both surface and groundwater (Brookfield and others, 2021) could be developed in conjunction with studies monitoring HABs occurrences in lotic and lentic waters.

Beyond Streamflow for Prediction of Ecologically Relevant Flow and Physical Metrics

Streamflow is important for predicting water and constituent conveyance to downstream areas as well as quality of ecological habitat (Poff and others, 1997; Arthington and others, 2010; Eng and others, 2013). However, streamflow is far from complete as a predictor of the physical controls on water-quality and ecological functions of river corridors (Dunne and others, 1998; National Research Council, 2002; Jones and Stanley, 2016; Appling and others, 2018). For example, there is a gap in estimating river travel time (and average reservoir residence time) along with associated mixing and oxygen reaeration processes, and flood inundation processes (Scott and others, 2019) which have an important role in models of water-quality and ecological functions of the Nation's rivers and reservoirs (Harvey and Gooseff, 2015; Harvey and others, 2019; Harvey and Schmadel, 2021).

Gap 2. Redox Processes Controlling Storage, Processing, and Release of N, P, Fe, As, and Other Contaminants

This gap involves redox processes controlling storage, processing, and release of N, P, Fe, As, and other contaminants. This includes physical drivers (for example, reaeration), geochemical (for example, contact with geochemically reducing sediments), and biological (for example, high labile carbon inputs) interactions in wastewater and septage ponds managed for water reuse, river-bank filtration zones, sediment retention ponds, reservoirs, and so forth.

Nitrogen, Phosphorus, Iron, and Arsenic Interactions in Wastewater and Septage Disposal

Nitrogen and P are common constituents in wastewater and septage disposal. The oxygen consuming capacity of those waters often results in anoxic zones in which P and geogenic As and Fe are solubilized and mobilized as a result of these disposal practices. If nitrate enters these zones, nitrate reduction can be coupled to Fe oxidation, leading to anoxic production of Fe oxides, which have the capacity to remove As, P, and other organic contaminants that can sorb onto the Fe oxides (Smith and others, 2017; Jamieson and others, 2018; Liu and others, 2019). Iron oxidation at oxic-anoxic boundaries can have the same effect, producing Fe oxides resulting in co-contaminant removal at the boundary interface. Thus, assessment of coupled processes is an important component for understanding co-contaminant transport and interaction in key water supply sources, wastewater disposal and reuse practices, wetlands, and groundwater-surface water interfaces. Studies could be done to determine rates of reaction, the sorption capacity, long-term fate of the sorbed constituents, and the extent to which Fe oxidation coupled to nitrate and (or) oxygen reduction occurs throughout the Nation's water supplies.

Gap 3. Interaction Between Nutrient Cycles and Contaminants of Emerging Concern

Interaction between nutrient cycles and contaminants of emerging concern (CECs), includes domestic and agricultural antibiotic effects on biogeochemistry, ecosystem metabolism, and co-contaminant fate and transport (such as microplastics effects on C and N processes).

Effects of Antibiotics (Domestic and Agricultural) on Water and Sediment Biogeochemistry and Co-Contaminant Fate and Transport

Natural and constructed wetlands are now used extensively across the United States as a means for mitigating nitrate losses to both surface and groundwater. While the use of wetlands as a treatment approach for nitrate-N is well known, the rates of nitrate removal and the ultimate fate of the nitrate-N are highly variable. Furthermore, N is not the sole contaminant that wetlands encounter. The presence of waterborne antibiotics, originating from both domestic and agricultural sources, is becoming increasingly common and can have an important effect on N cycle processes (Zou and others, 2019; Xu and others, 2020; Xu and others, 2021). The environmental consequences of these biologically active compounds on the fate and transport of N can potentially be significant but are only beginning to be investigated. Controlled laboratory and field studies could be done to document the effect of antibiotics on the relative rates of N cycling processes in aquatic systems.

The effects of antibiotics on microbial communities are complex. Antibiotics can have a direct effect on the microbial community structure and also on the development and transfer of antibiotic resistance genes (ARGs), which have been considered pollutants of concern in recent years (Pruden and others, 2006). Chemical pollution (for example, antibiotics, heavy metals, biocides), physicochemical factors (for example, DO, salinity, TDN [total dissolved N]), and human activities (for example, wastewater treatment plants, agriculture, hospitals) can have dramatic influences on the propagation of ARGs (Yang and others, 2018). Studies focusing on antibiotics and nutrients could include approaches for determining the responses of microbial communities.

Interaction Between Nitrogen Cycle Processes and Contaminants of Emerging Concern

A wide variety of CECs (defined here as including pharmaceuticals, agricultural products, and personal care products) and organic micropollutants (OMPs) occur in the Nation’s waters (Kolpin and others, 2002; Luo and others, 2014). Little is known about the effect of these chemicals on N cycle processes or, conversely, the potential for N redox reactions to degrade or assist in the degradation of CECs and OMPs in the environment. Those interactions that do occur could potentially be important for understanding the fate and transport of CECs and OMPs. Systematic studies including data reviews and lab experiments could be done to explore potential interactions. Nitrapyrin is one CEC that is known to inhibit nitrification and has been detected recently in rivers and streams in Iowa (Woodward and others, 2016). The presence of nitrapyrin and (or) its degradants in a stream could affect N speciation, depending on the nitrapyrin concentration, with concomitant effects on N transport, microbial community structure and function, and downstream eutrophication. Nitrification has also been shown to biotransform OMPs containing alkyl, aliphatic hydroxyl, ether, and sulfide functional groups as well as substituted aromatic rings and aromatic primary amines (Su and others, 2021).

Effect of Microplastics on Carbon, Nitrogen, and Phosphorus Biogeochemical Processes

Evidence suggests that micro and nanoplastics are abundantly present in the environment (Adomat and Grischek, 2021; Lenaker and others, 2021) and that they can affect biogeochemical processes in sediment and wetland N cycling (Seeley and others, 2020; Zaman and others, 2021). The USGS has the in-house expertise to carry out experimental dosing studies to examine the effect of microplastics on N cycle processes. A wide variety of parameters could be quantified using microcosms, mesocosms, or contained in situ chambers to assess N cycling, C cycling, greenhouse gas emissions, primary productivity (that is, relative to HABs), redox chemistry, macro fauna uptake, and trace element chemistry in the presence of microplastics. Added to that could be an examination of responses by different sediment or environment types or differences in other water quality parameters. These experimental studies are needed in the short-term to guide large-scale monitoring of plastic contaminants and to provide parameters and thresholds needed for modeling the effects on water quality.

Approaches to Address Gaps in Coupled Processes Affecting Water Availability

Below we provide four suggested approaches that potentially can be used to address the coupled-process gaps described in the previous section. The range of potential approaches are generally the same for each of the identified gaps; approaches are listed in order of scale, starting with microbial community-level assessment of the drivers, mechanistic studies of coupled processes, then working up to the ecosystem level using comprehensive measurements of coupled constituents at fixed stations, and finally to broader regional-scale assessments mapping N, P, C, and related eco-flow metrics across multiple scales. A final selection of approaches might involve one or more elements of each that will need to be tailored for any particular gap. A summary of gaps, approaches, and expected outcomes is provided in table B2.

Microbial Profiling

The use of metatranscriptomics (also known as “gene expression”) has become more common these days, going beyond determination of microbial community composition (metagenomics) and functional gene abundance (potential metabolism) to measuring gene expression to determine whether genes are being actively expressed or suppressed under specific environmental conditions. Whereas environmental deoxyribonucleic acid (DNA) sequencing can indicate the presence of a functional gene or a functional group of microbes, environmental ribonucleic acid (RNA) and gene expression (analysis of mRNA) indicates the active community and processes that are occurring within an environment, providing an assessment of the functional diversity of the community (Cristescu, 2019; Escalas and others, 2019; von Ammon and others, 2019; Cordier and others, 2021). These tools can be used to assess multiple biogeochemical processes and communities and link microbial functions to C, N, and P cycling processes. For example, coupling of chemical datasets with metatranscriptomics has been used to measure the response and coping mechanisms of the microbial community to xenobiotic stressors in sediments collected from the Detroit River (Falk and others, 2019).

Table B2. Summary of prioritized U.S. Geological Survey (USGS) knowledge gaps, approaches, and expected outcomes for water quality drivers of aquatic ecosystem health.

[C, carbon; N, nitrogen; P, phosphorus; HABs, harmful algal blooms; NO_3, nitrate; O, oxygen; Fe, iron; As, arsenic; CECs, contaminants of emerging concern; chl-a, chlorophyll a.]

Gap	Gap elements	Why	Approaches	Outcomes	References
Multi-factor N, P and labile C sources interacting with eco-flow drivers	Dominant sources of labile organic C. C, N, P biogeochemical processes that promote HABs and hypoxia. Need for ecologically relevant flow metrics beyond streamflow that predict eco-health (for example, river residence time, gas exchange, light attenuation).	C lability couples with N, P dynamics, affecting anoxia, HABs, and (or) NO_3 removal. River residence time, mixing, and reaeration effects of dissolved O availability, redox status, contaminant concentrations, and balance between primary productivity, respiration, and nutrient reactions that influence outcomes for eco-health.	Coupled process and machine learning modeling studies to predict impact and recovery times of biological community structure and function following physical or water-quality disturbances. Microbial profiling to link microbial community function with processing of N, P, contaminants.	More accurate assessment and modeling of HABs, hypoxia, water quality, and ecological functions.	Wickland and others, 2012; Gardner and others, 2017; Harvey and Schmadel, 2021.
Redox processes controlling storage, processing, and release of N, P, Fe, As, and other contaminants	Wastewater/septage disposal controlling downstream redox conditions and N, P, Fe, As cycling. Redox controls on mobility and bioavailability of N and P.	P, As, Fe can be mobilized or removed from wastewater sources, depending on nutrient concentrations, oxic and anoxic status.	"Fast mapping" of streambed redox status and related eco-flow drivers (river residence time) to build eco-metrics for model inputs.	Improved modeling of contaminants relative to drinking water sources and wastewater reuse.	Smith and others, 2017; Jamieson and others, 2018; Li and others, 2019.
Interaction between nutrient cycles and CECs	Effect of antibiotics on water/sediment biogeochemistry. Interactions with N cycle controlling CECs. Effect of microplastics on C and N biogeochemical processes.	Antibiotics affecting pollutants of concern; N redox reactions may degrade CECs; microplastics affect nutrient biogeochemistry, potentially affecting HABs formation.	Integrated eco-health metrics (sensor-based metabolism and remote sensing of turbidity and chl-a) combined with eco-flow metrics (for example, river residence time, gas exchange, light attenuation) as proxy indicators of water quality threats to ecological health. Comprehensive measurement of water-quality and eco-health predictors (dissolved oxygen in addition to temperature, nutrients, and specific conductance) to better serve stakeholder needs.	Improved prediction of N loads; improved understanding of CEC degradation; guide large-scale monitoring of microplastics	Pruden and others, 2006; Luo and others, 2014; Adomat and Grischek, 2021; Xu and others, 2021.

Metatranscriptomics in combination with metagenomics can be used to assess changes to microbial processing of nutrients and other contaminants resulting from agricultural runoff, fires, HABs, other chronic or extreme events, and provide information on linkages between physical, hydrologic, and chemical processes. It can be used to answer questions such as:

- Does repeated or seasonal exposure to certain chemicals, such as seasonal application of agricultural chemicals, eventually lead to adaptation by the microbial community?
- How does the function of the microbial community change in the presence of mixtures of contaminants?
- How quickly does the microbial community recover after extreme events, such as floods, wildfires, and so forth?

Mechanistic Studies of Coupled Processes

Quantitative information about kinetics of coupled processes and environmental factors that control process rates is essential information for predicting and understanding the function of the processes relative to water quality assessment and ecosystem health. Mechanistic studies of coupled processes can be conducted in controlled laboratory settings using freshly collected environmental materials (soil, sediment, water, biofilms, and so forth) to quantify potential rates of reactions, competition between various reaction couples, and responses to experimental manipulation (for example, temperature, substrate concentration, presence of other contaminants). These experiments control environmental variables that might occur across time and space within a watershed and quantify process response. Such results are extremely important for interpreting bulk changes in water and sediment geochemistry and for predicting effects of disturbances or other environmental changes. Field experiments, utilizing chemical and isotopic tracers, and carried out in conjunction with laboratory experiments, could provide invaluable information regarding in situ processes and rates. Reach-scale and hyporheic zone field experiments using conservative and reactive tracers have been used to measure denitrification rates (Böhlke and others, 2009; Harvey and others, 2013) as well as methane and nitrous oxide emissions (Smith and Böhlke, 2019) in streams heavily affected by agricultural inputs. Systematic experimental sampling across a watershed can incorporate process differences related to hydrology, landscape setting, groundwater inputs, sediment types, and contaminant exposures. Such an approach is also needed to integrate and scale up the effects of coupled processes from local to more regional settings, which is a major gap in our understanding of the role that coupled processes have in region-wide ecosystem health.

Comprehensive Measurements of Coupled Constituents at Fixed Stations

The USGS currently operates approximately 2,100 water quality stations around the country, with more to be added under the Next Generation Water Observing Stations (NGWOS) program. These stations can be equipped with a wide array of instrumentation that encompasses the range of parameters of interest in multi-constituent process studies, including multi-parameter sondes measuring water temperature, pH, specific conductance, dissolved O, turbidity, fluorescent dissolved organic matter (FDOM), and chlorophyll coupled with dissolved nitrate, phosphate, and carbon dioxide sensors. While NGWOS stations often have the purpose to integrate signals over large river basins, focus could also be directed towards comparing small watersheds with contrasting characteristics. Comprehensive measurements at both NGWOS and smaller scale watersheds could improve understanding and parameterization of watershed responses to N-P-C drivers. High frequency continuous sensor output measurements can help resolve processes such as metabolism, gas emissions, and so forth, which vary over short time scales (diel, high-flow, seasonal) that may not be resolved with discrete sampling protocols. Increasing and improving discrete sampling and analysis is also needed, however, to improve integrated constituent studies. Discrete sampling is essential for measuring important and informative chemical parameters (for example, isotopes of various constituents) that cannot be analyzed continuously or remotely. Added to this will be demands for new analytical capabilities as new contaminants of concern arise. The wealth of information collected from NGWOS stations and small watersheds can be leveraged with mapping and lab/field process studies in the two approaches described above and in the next approach to provide modelers with information crucial to model development, and to provide stakeholders with the data and interpretation necessary to make informed decisions.

Mapping of Nitrogen, Phosphorus, Carbon, and Related Eco-Flow Metrics Across Multiple Scales

The USGS NGWOS fixed-location water quality stations do not represent the full continuum of stream reach conditions (Crawford and others, 2016). A multi-scale approach could adequately address nutrient and C processing in rivers from the small watersheds hosting a single fixed-station to large basins hosting a number of fixed-stations scale. This scaling approach could provide modelers and stakeholders with an integrated “picture” of nutrient-C processing to facilitate model development and decision making. Better information about the geographic setting of freshwater resources is also needed to enhance our understanding of the scale, rate, and consequences of coupled biogeochemical reactions. The ongoing expansion of data collection including standard techniques along with rapidly developing new laboratory capabilities, high-frequency continuous sensor output and high-spatial resolution tools, remote sensing, and unmanned vehicles offers an unprecedented opportunity to describe aquatic resources more fully across the United States.

The tools that are currently available for estimation of river travel time and reservoir residence time throughout the United States are outdated and based on limited data sources (Harvey and Schmadel, 2021). Travel time estimates are essential for tracking how water-quality disturbances are propagated to downstream areas. Numerous stream tracer tests have been carried out in the past 60 years in the United States, but results have not been synthesized and analyzed to produce a model estimator for downstream propagation, dispersion and dilution, and for estimates of the time required for water-quality disturbances such as river spills to clear from the river corridor. Improved travel-time estimation can advance the prediction of water availability at any scale. Examples include (1) apportioning river contaminant loading and removal rates across watersheds, states, and regions; (2) incorporating contaminant legacy storage times and releases back to river corridors in water quality models; and (3) predicting downstream effects of water quality disturbance with early warning for downstream water users.

Remote sensing has been used to measure stream parameters such as width, depth, and streamflow, but recent advances in sensor technology and data processing are setting the stage for an expansion of remote sensing as a tool for mapping water quality from the scale of rivers down to a few meters (Tomsett and Leyland, 2019; Topp and others, 2020). Sensor data is becoming more available from platforms including satellites, manned aircraft, and uncrewed aerial vehicles (UAVs or drones). Published research has already shown the promise of remote sensing in modeling N and P (Lillesand and others, 1983; He and others, 2008; Torbick and others, 2013), dissolved O (Wang and others, 2004; Toming and others, 2016), and heavy metals (Choe and others, 2008; Fichot and others, 2016). Remote sensing has also been used to map chlorophyll a (Duan and others, 2007) and harmful cyanobacteria (Kudela and others, 2015; Oyama and others, 2015), total suspended sediment (Telmer and others, 2006; Riaza and others, 2012; Brando and others, 2015), colored dissolved organic matter (CDOM; a proxy for DOC and possibly methylmercury) (Griffin and others, 2011; Fichot and others, 2016), and water clarity (Olmanson and others, 2008; Sheela and others, 2011). While limitations with these technologies exist regarding repeatability, accuracy, and data processing, we are in a “golden age” of remote sensing as it applies to rivers (Tomsett and Leyland, 2019), and the USGS has the expertise to meet these challenges and be a leader in this field. Remote sensing of water quality needs continual improvement through ground-truthing measurements. This is another area where USGS has led the field, demonstrating the utility of high-speed high-resolution mapping of rivers for a number of water quality parameters (Crawford and others, 2015), including nitrate (Loken and others, 2018) and nitrous oxide (Turner and others, 2016). Boats can be equipped with water quality sensors that include temperature, conductance, O, pH, CDOM, turbidity, total algae, chlorophyll a, nitrate, ammonia, nitrous oxide, carbon dioxide, and methane. These boats equipped with multi-parameter sondes have the advantage of being able to map entire stretches of river such as the upper Mississippi (Crawford and others, 2016; Turner and others, 2016; Loken and others, 2018). The systems are mobile, allowing the mapping of river conditions across watersheds at various scales. They can also be used seasonally and on short notice, such as during storm or flooding events, HABs, and contamination events, and they can be timed to coincide with airborne and satellite overflights. They not only provide ground-truthing for remote sensing but can locate hot spots of coupled nutrient-C cycling such as wastewater disposal sites, drinking water treatment facilities, and tributary confluences and provide a river-scale method for calculating greenhouse gas emissions. Combined with the nutrient-C process studies described in previous sections above, this multi-scale data collection/mapping effort aligns with USGS WMA program goals for aquatic eco-health and water quality management moving into the future.

Timelines

Proposed timelines of prioritized USGS approaches to closing knowledge gaps for water quality drivers of aquatic ecosystem health are summarized in table B3.

Near-Term (2-Year) Advancements

1. Microbial Profiling: Incorporate DNA and RNA sampling at USGS Integrated Water Science (IWS) basins, perhaps the Illinois River Basin where anthropogenically-affected waters and sediments are evident. These studies could be combined with the exploratory mechanistic studies of coupled processes to assess how the microbial community adapts to changing conditions by exploiting new pathways and (or) employing stress-response mechanisms. A few USGS labs currently have the tools and expertise to extract and analyze samples for DNA, RNA, and gene abundance (for example, Laboratory and Analytical Services Division [LASD], Geology Energy and Minerals [GEM], and Upper Midwest Water Science Center [WSC]). Microarrays or geochips can simultaneously measure the expression level of thousands of functional genes important to biogeochemical processes or can identify gene changes in response to contaminants or other organisms.

2. Mechanistic Studies: Focus on C-N-P coupling in detail in a selected WMA IWS basin with exploratory experiments to test the effects of target CECs and OMPs found in the basin. Emphasis could be placed on deriving rate constants, temperature and other seasonal effects, and key locations for biogeochemical processing in the watershed (headwater vs. large channel streams, bed sediment vs. suspended sediment, gaining vs. losing groundwater reaches). This would include collaboration with modelers to begin incorporating results into process/transport models.

3. Comprehensive measurements of coupled constituents at fixed stations, focusing on IWS basins: Conduct regular sampling and analyses of high-priority N, C, and

Table B3. Timeline summary of prioritized U.S. Geological Survey (USGS) approaches to closing knowledge gaps for coupled nutrient-carbon cycle processes and related ecological-flow drivers of aquatic health.

[yr, year; DNA, deoxyribonucleic acid; RNA, ribonucleic acid; C, carbon, N, nitrogen; P, phosphorus; IWS, Integrated Water Science; CEC, contaminant of emerging concern; NGWOS, Next Generation Water Observing Stations.]

Advancements	Microbial profiling	Mechanistic studies of coupled processes	Coupled constituents at fixed stations	Mapping nutrients and carbon across multiple scales
Near-term (2-yr)	Include DNA/RNA sampling at an IWS basin site using microarrays to measure the microbial community response to environmental stressors.	Measure physicochemical parameters that affect C-N-P coupled rates at a select IWS basin site, incorporate results into process/transport models.	Identify reaches between fixed stations for intensive mechanistic studies, install "experimental sensors" at select stations, install wells to monitor groundwater inputs.	Analyze remote sensing-water quality data relationships to aid modeling, use new technological platforms to ground-truth models at select IWS basin site
Mid-term (2- to 5-yr)	Utilize predictive biology software to incorporate microbial physiology and community dynamics into reactive and process-based transport models.	Assess nutrient-CEC coupled processes, incorporate early results in models, select other IWS basins for study.	Carry out seasonal and diel studies using tracer tests to identify coupled biological and geochemical processes, permanently install experimental sensors at select stations.	Utilize the increased data and imagery collection by NGWOS stations to inform model predictions and stakeholders.
Long-term (10-yr)	Incorporate in situ automated molecular samplers into other IWS basin study sites	Expand lab quantification studies to other IWS basin sites, carry out field tracer tests to ground-truth process couple results and modeling efforts.	Expand capabilities to other NGWOS sites, incorporate measurement results into process-based models.	Use remote sensing and mapping platforms to map nutrients, C, and other parameters across multiple scales at all IWS basin sites

P constituents to complement and ground-truth sensor data at select fixed stations in NGWOS basins. Install "experimental sensors" that are not core NGWOS sensors at select fixed stations for testing and verification. Identify one or more reaches between fixed stations for intensive mechanistic studies to link sources and in-stream processes to observations at fixed stations across scales. Identify areas of regional groundwater inputs and design and install sampling wells and (or) multi-level samplers, along with streambed temperature arrays, at select input locations. This work could focus on IWS basins and can expand to other geographic areas of scientific interest.

4. Enhanced across-scale mapping of nutrients and carbon: Building on expanding USGS sensor networks, remote sensing offers low-hanging fruit including the AquaSat database (Ross and others, 2019), a set of 600,000 Landsat spectral reflectance measurements paired with field measurements of total suspended sediment, DOC, chlorophyll a, and secchi depth. This data set could be mined to examine remote sensing-water quality relationships, and aid in processing and modeling approaches. In addition, boats could be easily outfitted to run as high-speed measurement platforms to begin ground-truthing and creating heat maps for decision makers.

5. Assimilation and analysis of underutilized channel corridor data to estimate ecologically relevant flow and physical metrics beyond streamflow: Across-scale estimation of eco-flow metrics in all rivers and reservoirs of the Nation would be instrumental in coupled nutrient-carbon-and eco-flow modeling that makes use of the enhanced sensor networks and remote sensing described above in item 4 "Enhanced across-scale mapping of nutrients and carbon." Priority eco-flow drivers beyond streamflow include:

- River and reservoir travel time (residence time) as well as river and reservoir depth and volume as they vary with streamflow;
- longitudinal mixing by dispersion as well as vertical water mixing which influence dilution of constituent concentrations and contact with reactive bed sediments;
- turbulence and vertical mixing and its effects on oxygen reaeration which lessens metabolic stress on organisms and decreases the probability of hypoxia;
- off-channel exchange flows that lengthen the travel time and activate water-quality and ecological functions of backwaters, riparian wetlands, and floodplains, including providing low-flow habitat and prolonging low-flow

season return flows from near-stream (riparian and floodplain) storages;

- contaminant releases from legacy storage areas near or within the river corridor that are currently unaccounted for in water quality models are needed to prioritize land conservation versus instream restoration practices; and
- light availability within water column influenced by turbidity and riparian and topographic shading, substantially affects algal growth and potential for HABs.

Mid-Term (2- to 5-Year) Advancements

1. Microbial profiling: Work with modelers to incorporate molecular results into reactive transport models. Predictive biology software such as KBase (Arkin and others, 2018) could be used for modeling microbial physiology and community dynamics.
2. Mechanistic studies could include other process couples pertinent to the selected basin, such as exploring the effect of microplastics and antibiotics on N, P, and C cycling as well as targeted studies during HABs events. Initial modeling using the first 2-year results could be conducted and compared with basin water quality data to test the development of the modeling and provide feedback on laboratory measurements and approaches. Also, selection of additional IWS basin(s) for expanding the study could be conducted.
3. Comprehensive measurements of coupled constituents at fixed stations: Analysis of reaches between fixed stations selected for detailed study, which would include comprehensive seasonal and diel investigations with tracer tests to identify coupled biological and geochemical processes in water and sediments, biological communities, and physical attributes of reaches. Permanent installation of “experimental sensors” at select fixed stations after verification and ground-truthing.
4. Mapping of nutrients and carbon across multiple scales: There will likely be significant advances in remote sensing of water quality parameters in the next five years, hopefully with progress in technical capabilities and processing capacity. The potential exponential increase in available imagery over that time frame, combined with a new influx of data from NGWOS stations and fast limnology missions, could provide massive amounts of information with which to inform modelers and decision makers.

Long-Term (10-Year) Advancements

1. Microbial profiling: Include the incorporation of in situ samplers into ecosystem monitoring programs. As pointed out in Cordier and others, (2021, p. 2940):
2. “For aquatic ecosystems especially, the next breakthrough of this revolution is now expected to be the development and deployment of low-cost, automated and miniaturized in-situ environmental nucleic acids (eDNA and RNA) samplers (Carr and others, 2017; Gan and others, 2017). These may be integrated into autonomous instruments for broadscale and continuous ecosystem monitoring programmes (Brandt and others, 2016; Bohan and others, 2017; Aguzzi and others, 2019; Benway and others, 2019; Levin and others, 2019).”
3. Mechanistic studies could include expanding the laboratory quantification efforts to other IWS sites, conducting field tests with tracers to ground truth the combined laboratory/modeling results, more detailed examination of process couples that were deemed relevant in the earlier tests, and application of the model(s) to other data-rich sites where laboratory process assessments have not been conducted to test the suitability for extrapolation. Work with remote sensing and prediction models to coordinate experiments with HABs events.
4. Comprehensive measurements of coupled constituents at fixed stations: Expand capabilities and measurements to other NGWOS sites for incorporation into statistical and process-based models.
5. Mapping of nutrients and carbon across multiple scales: We anticipate that within 10 years the USGS could be in a position to take advantage of all remote sensing and high-speed mapping platforms.

Expected Outcomes

- Improved biogeochemical modelling from process studies that will lead to increased predictive capabilities;
- New tools and methodologies as a result of advances in remote sensing connectivity to aquatic eco-health metrics;
- Broad applicability and transferability across reach, basin, region, and national scales, beginning with a proof-of-concept approach in the Illinois River IWS basin;
- Serves WMA priorities through synergy with Integrated Watershed Availability Assessments (IWAA), IWP, and NGWOS program goals;
- Serves stakeholders and decision makers through improved mapping capabilities that help visualize annual, seasonal, and storm trends as well as identifying hot spots and other areas of concern.

References Cited

Abbott, B.W., Baranov, V., Mendoza-Lera, C., Nikolakopoulou, M., Harjung, A., Kolbe, T., Balasubramanian, M.N., Vaessen, T.N., Ciocca, F., Campeau, A., Wallin, M.B., Romeijn, P., Antonelli, M., Gonçalves, J., Datry, T., Laverman, A.M., de Dreuzy, J.-R., Hannah, D.M., Krause, S., Oldham, C., and Pinay, G., 2016, Using multi-tracer inference to move beyond single-catchment ecohydrology: Earth-Science Reviews, v. 160, p. 19–42, https://doi.org/10.1016/j.earscirev.2016.06.014.

Adomat, Y., and Grischek, T., 2021, Sampling and processing methods of microplastics in river sediments—A review: Science of the Total Environment, v. 758, article 143691, 15 p., https://doi.org/10.1016/j.scitotenv.2020.143691.

Aguzzi, J., Chatzievangelou, D., Marini, S., Fanelli, E., Danovaro, R., Flögel, S., Lebris, N., Juanes, F., De Leo, F.C., Del Rio, J., Thomsen, L., Costa, C., Riccobene, G., Tamburini, C., Lefevre, D., Gojak, C., Poulain, P.-M., Favali, P., Griffa, A., Purser, A., Cline, D., Edgington, D., Navarro, J., Stefanni, S., D'Hondt, S., Priede, I.G., Rountree, R., and Company, J.B., 2019, New high-tech flexible networks for the monitoring of deep-sea ecosystems: Environmental Science & Technology, v. 53, no. 12, p. 6616–6631, https://doi.org/10.1021/acs.est.9b00409.

Anderson, O.R., 2018, Evidence for coupling of the carbon and phosphorus biogeochemical cycles in freshwater microbial communities: Frontiers in Marine Science, v. 5, no. 20, 6 p., https://doi.org/10.3389/fmars.2018.00020.

Appling, A.P., Read, J.S., Winslow, L.A., Arroita, M., Bernhardt, E.S., Griffiths, N.A., Hall, R.O., Harvey, J.W., Heffernan, J.B., Stanley, E.H., Stets, E.G., and Yackulic, C.B., 2018, The metabolic regimes of 356 rivers in the United States: Scientific Data, v. 5, no. 1, article 180292, 14 p., https://doi.org/10.1038/sdata.2018.292.

Arkin, A.P., Cottingham, R.W., Henry, C.S., Harris, N.L., Stevens, R.L., Maslov, S., Dehal, P., Ware, D., Perez, F., Canon, S. , Sneddon, M.W., Henderson, M.L., Riehl, W.J., Murphy-Olson, D., Chan, S.Y., Kamimura, R.T., Kumari, S., Drake, M.M., Brettin, T.S., Glass, E.M., Chivian, D., Gunter, D., Weston, D.J., Allen, B.H., Baumohl, J., Best, A.A., Bowen, B., Brenner, S.E., Bun, C.C., Chandonia, J.-M., Chia, J.-M., Colasanti, R., Conrad, N., Davis, J.J., Davison, B.H., DeJongh, M., Devoid, S., Dietrich, E., Dubchak, I., Edirisinghe, J.N., Fang, G., Faria, J.P., Frybarger, P.M., Gerlach, W., Gerstein, M., Greiner, A., Gurtowski, J., Haun, H.L., He, F., Jain, R., Joachimiak, M.P., Keegan, K.P., Kondo, S., Kumar, V., Land, M.L., Meyer, F., Mills, M., Novichkov, P.S., Oh, T., Olsen, G.J., Olson, R., Parrello, B., Pasternak, S., Pearson, E., Poon, S.S., Price, G.A., Ramakrishnan, S., Ranjan, P., Ronald, P.C., Schatz, M.C., Seaver, S.M.D., Shukla, M., Sutormin, R.A., Syed, M.H., Thomason, J., Tintle, N.L., Wang, D., Xia, F., Yoo, H., Yoo, S., and Yu, D., 2018, KBase—The United States Department of Energy systems biology knowledgebase: Nature Biotechnology, v. 36, no. 7, p. 566–569, https://doi.org/10.1038/nbt.4163.

Arthington, A.H., Naiman, R.J., McClain, M.E., and Nilsson, C., 2010, Preserving the biodiversity and ecological services of rivers—New challenges and research opportunities: Freshwater Biology, v. 55, no. 1, p. 1–16, https://doi.org/10.1111/j.1365-2427.2009.02340.x.

Benway, H.M., Lorenzoni, L., White, A.E., Fiedler, B., Levine, N.M., Nicholson, D.P., DeGrandpre, M.D., Sosik, H.M., Church, M.J., O'Brien, T.D., Leinen, M., Weller, R.A., Karl, D.M., Henson, S.A., and Letelier, R.M., 2019, Ocean time series observations of changing marine ecosystems—An era of integration, synthesis, and societal applications: Frontiers in Marine Science, Ocean Observation, v. 6, no. 393, https://doi.org/10.3389/fmars.2019.00393.

Bohan, D.A., Vacher, C., Tamaddoni-Nezhad, A., Raybould, A., Dumbrell, A.J., and Woodward, G., 2017, Next-generation global biomonitoring: large-scale, automated reconstruction of ecological networks: Trends in Ecology & Evolution, v. 32, no. 7, p. 477-487.

Böhlke, J.K., Antweiler, R.C., Harvey, J.W., Laursen, A.E., Smith, L.K., Smith, R.L., and Voytek, M.A., 2009, Multi-scale measurements and modeling of denitrification in streams with varying flow and nitrate concentration in the upper Mississippi River basin, USA: Biogeochemistry, v. 93, no. 1, p. 117–141, https://doi.org/10.1007/s10533-008-9282-8.

Brando, V.E., Braga, F., Zaggia, L., Giardino, C., Bresciani, M., Matta, E., Bellafiore, D., Ferrarin, C., Maicu, F., Benetazzo, A., Bonaldo, D., Falcieri, F.M., Coluccelli, A., Russo, A., and Carniel, S., 2015, High-resolution satellite turbidity and sea surface temperature observations of river plume interactions during a significant flood event: Ocean Science, v. 11, no. 6, p. 909–920, https://doi.org/10.5194/os-11-909-2015.

Brandt, A., Gutt, J., Hildebrandt, M., Pawlowski, J., Schwendner, J., Soltwedel, T., and Thomsen, L., 2016, Cutting the umbilical—New technological perspectives in benthic deep-sea research: Journal of Marine Science and Engineering, v. 4, no. 2, 27 p., https://doi.org/10.3390/jmse4020036.

Brookfield, A.E., Hansen, A.T., Sullivan, P.L., Czuba, J.A., Kirk, M.F., Li, L., Newcomer, M.E., and Wilkinson, G., 2021, Predicting algal blooms—Are we overlooking groundwater?: Science of the Total Environment, v. 769, article 144442, 15 p., https://doi.org/10.1016/j.scitotenv.2020.144442.

Bruggeman, J., and Bolding, K., 2014, A general framework for aquatic biogeochemical models: Environmental Modelling & Software, v. 61, p. 249–265, https://doi.org/10.1016/j.envsoft.2014.04.002.

Canadell, J.G., Le Quéré, C., Raupach, M.R., Field, C.B., Buitenhuis, E.T., Ciais, P., Conway, T.J., Gillett, N.P., Houghton, R.A., and Marland, G., 2007, Contributions to accelerating atmospheric CO2 growth from economic activity, carbon intensity, and efficiency of natural sinks: Proceedings of the National Academy of Sciences, v. 104, no. 47, p. 18866–18870, https://doi.org/10.1073/pnas.0702737104.

Carr, C.E., Mojarro, A., Hachey, J., Saboda, K., Tani, J., Bhattaru, S.A., Smith, A., Pontefract, A., Zuber, M.T., Doebler, R., Brown, M., Herrington, K., Talbot, R., Nguyen, V., Bailey, R., Ferguson, T., Finney, M., Church, G., and Ruvkun, G., 2017, Towards in situ sequencing for life detection, in 2017 IEEE Aerospace Conference, Big Sky, Montana, March 4–11, 2017: Institute of Electrical and Electronics Engineers (IEEE), p. 1–18, https://doi.org/10.1109/AERO.2017.7943896.

Chen, X., Wang, K., Li, X., Qiao, Y., Dong, K., and Yang, L., 2021, Microcystis blooms aggravate the diurnal alternation of nitrification and nitrate reduction in the water column in Lake Taihu: Science of the Total Environment, v. 767, article 144884, 9 p., https://doi.org/10.1016/j.scitotenv.2020.144884.

Choe, E., van der Meer, F., van Ruitenbeek, F., van der Werff, H., de Smeth, B., and Kim, K.-W., 2008, Mapping of heavy metal pollution in stream sediments using combined geochemistry, field spectroscopy, and hyperspectral remote sensing—A case study of the Rodalquilar mining area, SE Spain: Remote Sensing of Environment, v. 112, no. 7, p. 3222–3233, https://doi.org/10.1016/j.rse.2008.03.017.

Community Coordinating Group on Integrated Hydro-Terrestrial Modeling, 2020, Integrated Hydro-terrestrial modeling—Development of a National Capability, in Report of an Interagency workshop, September 4–6, 2019: National Science Foundation, U.S. Department of Energy, and U.S. Geological Survey, 180 p., https://doi.org/10.25584/09102020/1659275.

Cordier, T., Alonso-Sáez, L., Apothéloz-Perret-Gentil, L., Aylagas, E., Bohan, D.A., Bouchez, A., Chariton, A., Creer, S., Frühe, L., Keck, F., Keeley, N., Laroche, O., Leese, F., Pochon, X., Stoeck, T., Pawlowski, J., and Lanzén, A., 2021, Ecosystems monitoring powered by environmental genomics—A review of current strategies with an implementation roadmap: Molecular Ecology, v. 30, no. 13 (special issue), p. 2937–2958, https://doi.org/10.1111/mec.15472.

Crawford, J.T., Loken, L.C., Casson, N.J., Smith, C., Stone, A.G., and Winslow, L.A., 2015, High-Speed Limnology—Using advanced sensors to investigate spatial variability in biogeochemistry and hydrology: Environmental Science & Technology, v. 49, no. 1, p. 442–450, https://doi.org/10.1021/es504773x.

Crawford, J.T., Loken, L.C., Stanley, E.H., Stets, E.G., Dornblaser, M.M., and Striegl, R.G., 2016, Basin scale controls on CO2 and CH4 emissions from the Upper Mississippi River: Geophysical Research Letters, v. 43, no. 5, p. 1973–1979, https://doi.org/10.1002/2015GL067599.

Cristescu, M.E., 2019, Can environmental RNA revolutionize biodiversity science?: Trends in Ecology & Evolution, v. 34, no. 8, p. 694–697, https://doi.org/10.1016/j.tree.2019.05.003.

Duan, H., Zhang, Y., Zhang, B., Song, K., and Wang, Z., 2007, Assessment of chlorophyll-a concentration and trophic state for Lake Chagan using Landsat TM and field spectral data: Environmental Monitoring and Assessment, v. 129, no. 1, p. 295–308, https://doi.org/10.1007/s10661-006-9362-y.

Dunne, T., Mertes, L.A.K., Meade, R.H., Richey, J.E., and Forsberg, B.R., 1998, Exchanges of sediment between the flood plain and channel of the Amazon River in Brazil: Geological Society of America (GSA) Bulletin, v. 110, no. 4, p. 450–467, https://doi.org/10.1130/0016-7606(1998)110%3C0450:EOSBTF%3E2.3.CO;2.

Eng, K., Wolock, D.M., and Carlisle, D.M., 2013, River flow changes related to land and water management practices across the conterminous United States: Science of the Total Environment, v. 463–464, p. 414–422, https://doi.org/10.1016/j.scitotenv.2013.06.001.

Escalas, A., Hale, L., Voordeckers, J.W., Yang, Y., Firestone, M.K., Alvarez-Cohen, L., and Zhou, J., 2019, Microbial functional diversity—From concepts to applications: Ecology and Evolution, v. 9, no. 20, p. 12000–12016, https://doi.org/10.1002/ece3.5670.

Falk, N., Reid, T., Skoyles, A., Grgicak-Mannion, A., Drouillard, K., and Weisener, C.G., 2019, Microbial metatranscriptomic investigations across contaminant gradients of the Detroit River: Science of the Total Environment, v. 690, p. 121–131, https://doi.org/10.1016/j.scitotenv.2019.06.451.

Falkowski, P.G., Fenchel, T., and Delong, E.F., 2008, The microbial engines that drive Earth's biogeochemical cycles: Science, v. 320, no. 5879, p. 1034–1039, https://doi.org/10.1126/science.1153213.

Fichot, C.G., Downing, B.D., Bergamaschi, B.A., Windham-Myers, L., Marvin-DiPasquale, M., Thompson, D.R., and Gierach, M.M., 2016, High-resolution remote sensing of water quality in the San Francisco Bay–Delta Estuary: Environmental Science & Technology, v. 50, no. 2, p. 573–583, https://doi.org/10.1021/acs.est.5b03518.

Finzi, A.C., Austin, A.T., Cleland, E.E., Frey, S.D., Houlton, B.Z., and Wallenstein, M.D., 2011, Responses and feedbacks of coupled biogeochemical cycles to climate change: examples from terrestrial ecosystems: Frontiers in Ecology and the Environment, v. 9, no. 1, p. 61–67, https://doi.org/10.1890/100001.

Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., and Sutton, M.A., 2008, Transformation of the nitrogen cycle—Recent trends, questions, and potential solutions: Science, v. 320, no. 5878, p. 889–892, https://doi.org/10.1126/science.1136674.

Gan, W., Gu, Y., Han, J., Li, C.-x., Sun, J., and Liu, P., 2017, Chitosan-modified filter paper for nucleic acid extraction and "in situ PCR" on a thermoplastic microchip: Analytical Chemistry, v. 89, no. 6, p. 3568–3575, https://doi.org/10.1021/acs.analchem.6b04882.

Gardner, W.S., Newell, S.E., McCarthy, M.J., Hoffman, D.K., Lu, K., Lavrentyev, P.J., Hellweger, F.L., Wilhelm, S.W., Liu, Z., Bruesewitz, D.A., and Paerl, H.W., 2017, Community biological ammonium demand—A conceptual model for cyanobacteria blooms in eutrophic lakes: Environmental Science & Technology, v. 51, no. 14, p. 7785–7793, https://doi.org/10.1021/acs.est.6b06296.

Gilbert, N., 2009, Environment—The disappearing nutrient: Nature, v. 461, no. 7265, p. 716–718, https://doi.org/10.1038/461716a.

Glibert, P.M., 2017, Eutrophication, harmful algae and biodiversity—Challenging paradigms in a world of complex nutrient changes: Marine Pollution Bulletin, v. 124, no. 2, p. 591–606, https://doi.org/10.1016/j.marpolbul.2017.04.027.

Graham, E.B., Knelman, J.E., Schindlbacher, A., Siciliano, S., Breulmann, M., Yannarell, A., Beman, J.M., Abell, G., Philippot, L., Prosser, J., Foulquier, A., Yuste, J.C., Glanville, H.C., Jones, D.L., Angel, R., Salminen, J., Newton, R.J., Bürgmann, H., Ingram, L.J., Hamer, U., Siljanen, H.M.P., Peltoniemi, K., Potthast, K., Bañeras, L., Hartmann, M., Banerjee, S., Yu, R.-Q., Nogaro, G., Richter, A., Koranda, M., Castle, S.C., Goberna, M., Song, B., Chatterjee, A., Nunes, O.C., Lopes, A.R., Cao, Y., Kaisermann, A., Hallin, S., Strickland, M.S., Garcia-Pausas, J., Barba, J., Kang, H., Isobe, K., Papaspyrou, S., Pastorelli, R., Lagomarsino, A., Lindström, E.S., Basiliko, N., and Nemergut, D.R., 2016, Microbes as engines of ecosystem function—When does community structure enhance predictions of ecosystem processes?: Frontiers in Microbiology, v. 7, no. 214, 10 p., https://doi.org/10.3389/fmicb.2016.00214.

Green, M.A., Waldbusser, G.G., Reilly, S.L., Emerson, K., and O’Donnell, S., 2009, Death by dissolution—Sediment saturation state as a mortality factor for juvenile bivalves: Limnology and Oceanography, v. 54, no. 4, p. 1037–1047, https://doi.org/10.4319/lo.2009.54.4.1037.

Griffin, C.G., Frey, K.E., Rogan, J., and Holmes, R.M., 2011, Spatial and interannual variability of dissolved organic matter in the Kolyma River, East Siberia, observed using satellite imagery: Journal of Geophysical Research: Biogeosciences, v. 116, no. G3, 12 p., https://doi.org/10.1029/2010JG001634.

Harvey, J.W., Böhlke, J.K., Voytek, M.A., Scott, D., and Tobias, C.R., 2013, Hyporheic zone denitrification—Controls on effective reaction depth and contribution to whole-stream mass balance: Water Resources Research, v. 49, no. 10, p. 6298–6316, https://doi.org/10.1002/wrcr.20492.

Harvey, J., Gomez-Velez, J., Schmadel, N., Scott, D., Boyer, E., Alexander, R., Eng, K., Golden, H., Kettner, A., Konrad, C., Moore, R., Pizzuto, J., Schwarz, G., Soulsby, C., and Choi, J., 2019, How hydrologic connectivity regulates water quality in river corridors: Journal of the American Water Resources Association, v. 55, no. 2, p. 369–381, https://doi.org/10.1111/1752-1688.12691.

Harvey, J., and Gooseff, M., 2015, River corridor science: Hydrologic exchange and ecological consequences from bedforms to basins: Water Resources Research, v. 51, no. 9, p. 6893–6922, https://doi.org/10.1002/2015WR017617.

Harvey, J.W., and Schmadel, N.M., 2021, The river corridor’s evolving connectivity of lotic and lentic waters: Frontiers in Water, v. 2, no. 70, article 580727, 17 p., https://doi.org/10.3389/frwa.2020.580727.

He, W., Chen, S., Liu, X., and Chen, J., 2008, Water quality monitoring in a slightly-polluted inland water body through remote sensing—Case study of the Guanting Reservoir in Beijing, China: Frontiers of Environmental Science & Engineering in China, v. 2, no. 2, p. 163–171, https://doi.org/10.1007/s11783-008-0027-7.

Howarth, R., Chan, F., Conley, D.J., Garnier, J., Doney, S.C., Marino, R., and Billen, G., 2011, Coupled biogeochemical cycles—Eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems: Frontiers in Ecology and the Environment, v. 9, no. 1, p. 18–26, https://doi.org/10.1890/100008.

Jamieson, J., Prommer, H., Kaksonen, A.H., Sun, J., Siade, A.J., Yusov, A., and Bostick, B., 2018, Identifying and quantifying the intermediate processes during nitrate-dependent iron(II) oxidation: Environmental Science & Technology, v. 52, no. 10, p. 5771–5781, https://doi.org/10.1021/acs.est.8b01122.

Jones, J.B., and Stanley, E.H., eds., 2016, Stream ecosystems in a changing environment: Academic Press, 548 p.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., and Buxton, H.T., 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000—A National Reconnaissance: Environmental Science & Technology, v. 36, no. 6, p. 1202–1211, https://doi.org/10.1021/es011055j.

Kudela, R.M., Palacios, S.L., Austerberry, D.C., Accorsi, E.K., Guild, L.S., and Torres-Perez, J., 2015, Application of hyperspectral remote sensing to cyanobacterial blooms in inland waters: Remote Sensing of Environment, v. 167, p. 196–205, https://doi.org/10.1016/j.rse.2015.01.025.

Lenaker, P.L., Corsi, S.R., and Mason, S.A., 2021, Spatial distribution of microplastics in surficial benthic sediment of Lake Michigan and Lake Erie: Environmental Science & Technology, v. 55, no. 1, p. 373–384, https://doi.org/10.1021/acs.est.0c06087.

Levin, L.A., Bett, B.J., Gates, A.R., Heimbach, P., Howe, B.M., Janssen, F., McCurdy, A., Ruhl, H.A., Snelgrove, P., Stocks, K.I., Bailey, D., Baumann-Pickering, S., Beaverson, C., Benfield, M.C., Booth, D.J., Carreiro-Silva, M., Colaço, A., Eblé, M.C., Fowler, A.M., Gjerde, K.M., Jones, D.O.B., Katsumata, K., Kelley, D., Le Bris, N., Leonardi, A.P., Lejzerowicz, F., Macreadie, P.I., McLean, D., Meitz, F., Morato, T., Netburn, A., Pawlowski, J., Smith, C.R., Sun, S., Uchida, H., Vardaro, M.F., Venkatesan, R., and Weller, R.A., 2019, Global observing needs in the deep ocean: Frontiers in Marine Science, v. 6, no. 241, https://doi.org/10.3389/fmars.2019.00241.

Li, X., Sardans, J., Hou, L., Gao, D., Liu, M., and Peñuelas, J., 2019, Dissimilatory nitrate/nitrite reduction processes in river sediments across climatic gradient—Influences of biogeochemical controls and climatic temperature regime: Journal of Geophysical Research: Biogeosciences, v. 124, no. 7, p. 2305–2320, https://doi.org/10.1029/2019JG005045.

Lillesand, T.M., Johnson, W.L., Deuell, R.L., Lindstrom, O.M., and Meisner, D.E., 1983, Use of Landsat data to predict the trophic state of Minnesota lakes: Photogrammetric Engineering and Remote Sensing, v. 49, no. 2., p. 219–229, https://www.asprs.org/wp-content/uploads/pers/1983journal/feb/1983_feb_219-229.pdf.

Liu, T., Chen, D., Luo, X., Li, X., and Li, F., 2019, Microbially mediated nitrate-reducing Fe(II) oxidation—Quantification of chemodenitrification and biological reactions: Geochimica et Cosmochimica Acta, v. 256 (special issue), p. 97–115, https://doi.org/10.1016/j.gca.2018.06.040.

Loken, L.C., Crawford, J.T., Dornblaser, M.M., Striegl, R.G., Houser, J.N., Turner, P.A., and Stanley, E.H., 2018, Limited nitrate retention capacity in the Upper Mississippi River: Environmental Research Letters, v. 13, no. 7, article 074030, 13 p., https://doi.org/10.1088/1748-9326/aacd51.

Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., and Wang, X.C., 2014, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment: Science of the Total Environment, v. 473–474, p. 619–641, https://doi.org/10.1016/j.scitotenv.2013.12.065.

Marvin-DiPasquale, M., Lutz, M.A., Brigham, M.E., Krabbenhoft, D.P., Aiken, G.R., Orem, W.H. and Hall, B.D., 2009, Mercury cycling in stream ecosystems, 2—Benthic methylmercury production and bed sediment—Pore water partitioning: Environmental science & technology, v. 43, no. 8, p. 2726–2732, https://doi.org/10.1021/es802698v.

McClain, M.E., Boyer, E.W., Dent, C.L., Gergel, S.E., Grimm, N.B., Groffman, P.M., Hart, S.C., Harvey, J.W., Johnston, C.A., Mayorga, E., McDowell, W.H., and Pinay, G., 2003, Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems: Ecosystems, v. 6, no. 4, p. 301–312, https://doi.org/10.1007/s10021-003-0161-9.

National Research Council, 2002, Riparian Areas—Functions and Strategies for Management: Washington, D.C., The National Academies Press, 448 p. [Available at https://doi.org/10.17226/10327.]

Olmanson, L.G., Bauer, M.E., and Brezonik, P.L., 2008, A 20-year Landsat water clarity census of Minnesota's 10,000 lakes: Remote Sensing of Environment, v. 112, no. 11 (special issue), p. 4086–4097, https://doi.org/10.1016/j.rse.2007.12.013.

Oyama, Y., Matsushita, B., and Fukushima, T., 2015, Distinguishing surface cyanobacterial blooms and aquatic macrophytes using Landsat/TM and ETM+ shortwave infrared bands: Remote Sensing of Environment, v. 157, p. 35–47, https://doi.org/10.1016/j.rse.2014.04.031.

Poff, N.L., Allan, J.D., Bain, M.B., Karr, J.R., Prestegaard, K.L., Richter, B.D., Sparks, R.E., and Stromberg, J.C., 1997, The natural flow regime: BioScience, v. 47, no. 11, p. 769–784, https://doi.org/10.2307/1313099.

Pruden, A., Pei, R., Storteboom, H., and Carlson, K.H., 2006, Antibiotic resistance genes as emerging contaminants—Studies in Northern Colorado: Environmental Science & Technology, v. 40, no. 23, p. 7445–7450, https://doi.org/10.1021/es060413l.

Riaza, A., Buzzi, J., García-Meléndez, E., Vázquez, I., Bellido, E., Carrère, V., and Müller, A., 2012, Pyrite mine waste and water mapping using Hymap and Hyperion hyperspectral data: Environmental Earth Sciences, v. 66, no. 7, p. 1957–1971, https://doi.org/10.1007/s12665-011-1422-0.

Ross, M.R.V., Topp, S.N., Appling, A.P., Yang, X., Kuhn, C., Butman, D., Simard, M., and Pavelsky, T.M., 2019, AquaSat—A data set to enable remote sensing of water quality for inland waters: Water Resources Research, v. 55, no. 11, p. 10012–10025, https://doi.org/10.1029/2019WR024883.

Schlesinger, W.H., 1997, Biogeochemistry—An Analysis of Global Change (2d ed.): Academic Press, 588 p.

Schlesinger, W.H., Cole, J.J., Finzi, A.C., and Holland, E.A., 2011, Introduction to coupled biogeochemical cycles: Frontiers in Ecology and the Environment, v. 9, no. 1, p. 5–8, https://doi.org/10.1890/090235.

Schmadel, N.M., Harvey, J.W., Schwarz, G.E., Alexander, R.B., Gomez-Velez, J.D., Scott, D., and Ator, S.W., 2019, Small ponds in headwater catchments are a dominant influence on regional nutrient and sediment budgets: Geophysical Research Letters, v. 46, no. 16, p. 9669–9677, https://doi.org/10.1029/2019GL083937.

Scott, D.T., Gomez-Velez, J.D., Jones, C.N., and Harvey, J.W., 2019, Floodplain inundation spectrum across the United States: Nature Communications, v. 10, no. 1, article 5194, 8 p., https://doi.org/10.1038/s41467-019-13184-4.

Seitzinger, S.P., 1988, Denitrification in freshwater and coastal marine ecosystems—Ecological and geochemical significance: Limnology and Oceanography, v. 33, no. 4, part 2, p. 702–724, https://doi.org/10.4319/lo.1988.33.4part2.0702.

Seeley, M.E., Song, B., Passie, R., and Hale, R.C., 2020, Microplastics affect sedimentary microbial communities and nitrogen cycling: Nature Communications, v. 11, no. 1, article 2372, 10 p., https://doi.org/10.1038/s41467-020-16235-3.

Seitzinger, S.P., 1988, Denitrification in freshwater and coastal marine ecosystems—Ecological and geochemical significance: Limnology and Oceanography, v. 33, no. 4, part 2, p. 702–724, https://doi.org/10.4319/lo.1988.33.4part2.0702.

Sheela, A.M., Letha, J., Joseph, S., Ramachandran, K.K., and Sanalkumar, S.P., 2011, Trophic state index of a lake system using IRS (P6-LISS III) satellite imagery: Environmental Monitoring and Assessment, v. 177, no. 1, p. 575–592, https://doi.org/10.1007/s10661-010-1658-2.

Smith, R.L., and Böhlke, J.K., 2019, Methane and nitrous oxide temporal and spatial variability in two midwestern USA streams containing high nitrate concentrations: Science of the Total Environment, v. 685, p. 574–588, https://doi.org/10.1016/j.scitotenv.2019.05.374.

Smith, R.L., Kent, D.B., Repert, D.A., and Böhlke, J.K., 2017, Anoxic nitrate reduction coupled with iron oxidation and attenuation of dissolved arsenic and phosphate in a sand and gravel aquifer: Geochimica et Cosmochimica Acta, v. 196, p. 102–120, https://doi.org/10.1016/j.gca.2016.09.025.

Smith, R.L., Repert, D.A., Stoliker, D.L., Kent, D.B., Song, B., LeBlanc, D.R., McCobb, T.D., Böhlke, J.K., Hyun, S.P., and Moon, H.S., 2019, Seasonal and spatial variation in the location and reactivity of a nitrate-contaminated groundwater discharge zone in a lakebed: Journal of Geophysical Research: Biogeosciences, v. 124, no. 7, p. 2186–2207, https://doi.org/10.1029/2018JG004635.

Stackpoole, S.M., Stets, E.G., and Sprague, L.A., 2019, Variable impacts of contemporary versus legacy agricultural phosphorus on US river water quality: Proceedings of the National Academy of Sciences, v. 116, no. 41, p. 20562–20567, accessed mm dd, yyyy, at https://doi.org/10.1073/pnas.1903226116.

Sterner, R., and Elser, J., 2002, Ecological stoichiometry—The biology of elements from molecules to the biosphere: Princeton, Princeton University Press, 464 p. [Available at https://doi.org/10.1515/9781400885695.]

Stets, E.G., Sprague, L.A., Oelsner, G.P., Johnson, H.M., Murphy, J.C., Ryberg, K., Vecchia, A.V., Zuellig, R.E., Falcone, J.A., and Riskin, M.L., 2020, Landscape drivers of dynamic change in water quality of U.S. rivers: Environmental Science & Technology, v. 54, no. 7, p. 4336–4343, https://doi.org/10.1021/acs.est.9b05344.

Strauss, E.A., and Lamberti, G.A., 2000, Regulation of nitrification in aquatic sediments by organic carbon: Limnology and Oceanography, v. 45, no. 8, p. 1854–1859, https://doi.org/10.4319/lo.2000.45.8.1854.

Strauss, E.A., and Lamberti, G.A., 2002, Effect of dissolved organic carbon quality on microbial decomposition and nitrification rates in stream sediments: Freshwater Biology, v. 47, no. 1, p. 65–74, https://doi.org/10.1046/j.1365-2427.2002.00776.x.

Su, Q., Schittich, A.-R., Jensen, M.M., Ng, H., and Smets, B.F., 2021, Role of ammonia oxidation in organic micropollutant transformation during wastewater treatment—Insights from molecular, cellular, and community level observations: Environmental Science & Technology, v. 55, no. 4, p. 2173–2188, https://doi.org/10.1021/acs.est.0c06466.

Suen, J.P. and Eheart, J.W., 2006, Reservoir management to balance ecosystem and human needs—Incorporating the paradigm of the ecological flow regime: Water Resources Research, v. 42, no. 3, https://doi.org/10.1029/2005WR004314.

Taguchi, V.J., Olsen, T.A., Natarajan, P., Janke, B.D., Gulliver, J.S., Finlay, J.C., and Stefan, H.G., 2020, Internal loading in stormwater ponds as a phosphorus source to downstream waters: Limnology and Oceanography Letters, v. 5, no. 4, p. 322–330, https://doi.org/10.1002/lol2.10155.

Telmer, K., Costa, M., Angélica, R.S., Araujo, E.S., and Maurice, Y., 2006, The source and fate of sediment and mercury in the Tapajós River, Pará, Brazilian Amazon—Ground- and space-based evidence: Journal of Environmental Management, v. 81, no. 2, p. 101–113, https://doi.org/10.1016/j.jenvman.2005.09.027.

Tesoriero, A.J., Erickson, M.L., Conaway, C.H., Tomaszewski, E.J., and Green, C.T., 2024, Knowledge gaps and opportunities for understanding water-quality processes affecting water availability for beneficial uses: U.S. Geological Survey Open-File Report 2023–1086, 81 p., https://doi.org/10.3133/ofr20231086.

Tomsett, C., and Leyland, J., 2019, Remote sensing of river corridors—A review of current trends and future directions: River Research and Applications, v. 35, no. 7, p. 779–803, https://doi.org/10.1002/rra.3479.

Topp, S.N., Pavelsky, T.M., Jensen, D., Simard, M., and Ross, M.R.V., 2020, Research trends in the use of remote sensing for inland water quality science—Moving towards multidisciplinary applications: Water, v. 12, no. 1, article 169, 34 p., at https://doi.org/10.3390/w12010169.

Torbick, N., Hession, S., Hagen, S., Wiangwang, N., Becker, B., and Qi, J., 2013, Mapping inland lake water quality across the Lower Peninsula of Michigan using Landsat TM imagery: International Journal of Remote Sensing, v. 34, no. 21, p. 7607–7624, https://doi.org/10.1080/01431161.2013.822602.

Turner, P.A., Griffis, T.J., Baker, J.M., Lee, X., Crawford, J.T., Loken, L.C., and Venterea, R.T., 2016, Regional-scale controls on dissolved nitrous oxide in the Upper Mississippi River: Geophysical Research Letters, v. 43, no. 9, p. 4400–4407, https://doi.org/10.1002/2016GL068710.

U.S. Environmental Protection Agency [EPA], 2017, National Summary of State Information: U.S. Environmental Protection Agency, accessed January 2021, at https://iaspub.epa.gov/waters10/attains_nation_cy.control. [Also available at https://www.epa.gov/waterdata/attains]

Toming, K., Kutser, T., Laas, A., Sepp, M., Paavel, B., and Nõges, T., 2016, First experiences in mapping lake water quality parameters with Sentinel-2 MSI imagery: Remote Sensing, v. 8, no. 8 (special issue), article. 640, 14 p., https://doi.org/10.3390/rs8080640.

von Ammon, U., Wood, S.A., Laroche, O., Zaiko, A., Lavery, S.D., Inglis, G.J., and Pochon, X., 2019, Linking environmental DNA and RNA for improved detection of the marine invasive fanworm Sabella spallanzanii: Frontiers in Marine Science, v. 6, no. 621, https://doi.org/10.3389/fmars.2019.00621.

Wang, Y., Hu, Y., Yang, C., Wang, Q., and Jiang, D., 2019, Variations of DOM quantity and compositions along WWTPs-river-lake continuum—Implications for watershed environmental management: Chemosphere, v. 218, p. 468–476, https://doi.org/10.1016/j.chemosphere.2018.11.037.

Wang, Y., Xia, H., Fu, J., and Sheng, G., 2004, Water quality change in reservoirs of Shenzhen, China—Detection using LANDSAT/TM data: Science of the Total Environment, v. 328, nos. 1–3, p. 195–206, https://doi.org/10.1016/j.scitotenv.2004.02.020.

Weisener, C., Lee, J., Chaganti, S.R., Reid, T., Falk, N., and Drouillard, K., 2017, Investigating sources and sinks of N_2O expression from freshwater microbial communities in urban watershed sediments: Chemosphere, v. 188, p. 697–705, https://doi.org/10.1016/j.chemosphere.2017.09.036.

Wickland, K.P., Aiken, G.R., Butler, K., Dornblaser, M.M., Spencer, R.G.M., and Striegl, R.G., 2012, Biodegradability of dissolved organic carbon in the Yukon River and its tributaries—Seasonality and importance of inorganic nitrogen: Global Biogeochemical Cycles, v. 26, no. 4, 14 p., https://doi.org/10.1029/2012GB004342.

Woodward, E.E., Edwards, T.M., Givens, C.E., Kolpin, D.W., and Hladik, M.L., 2021, Widespread use of the nitrification inhibitor nitrapyrin—Assessing benefits and costs to agriculture, ecosystems, and environmental health: Environmental Science & Technology, v. 55, no. 3, p. 1345–1353, https://doi.org/10.1021/acs.est.0c05732.

Woodward, E.E., Hladik, M.L., and Kolpin, D.W., 2016, Nitrapyrin in streams—The first study documenting off-field transport of a nitrogen stabilizer compound: Environmental Science & Technology Letters, v. 3, no. 11, p. 387–392, https://doi.org/10.1021/acs.estlett.6b00348.

Xia, X., Liu, T., Yang, Z., Michalski, G., Liu, S., Jia, Z., and Zhang, S., 2017, Enhanced nitrogen loss from rivers through coupled nitrification-denitrification caused by suspended sediment: Science of The Total Environment, v. 579, p. 47–59, https://doi.org/10.1016/j.scitotenv.2016.10.181.

Xu, H., Lu, G., and Xue, C., 2020, Effects of sulfamethoxazole and 2-ethylhexyl-4-methoxycinnamate on the dissimilatory nitrate reduction processes and N2O release in sediments in the Yarlung Zangbo River: International Journal of Environmental Research and Public Health, v. 17, no. 6, article 1822, 15 p., https://doi.org/10.3390/ijerph17061822.

Xu, L., Zhang, H., Xiong, P., Zhu, Q., Liao, C., and Jiang, G., 2021, Occurrence, fate, and risk assessment of typical tetracycline antibiotics in the aquatic environment—A review: Science of the Total Environment, v. 753, article 141975, 17 p., https://doi.org/10.1016/j.scitotenv.2020.141975.

Yang, Y., Song, W., Lin, H., Wang, W., Du, L., and Xing, W., 2018, Antibiotics and antibiotic resistance genes in global lakes—A review and meta-analysis: Environment International, v. 116, p. 60–73, https://doi.org/10.1016/j.envint.2018.04.011.

Zaman, M., Kim, M., and Nakhla, G., 2021, Simultaneous nitrification-denitrifying phosphorus removal (SNDPR) at low DO for treating carbon-limited municipal wastewater: Science of the Total Environment, v. 760, article 143387, 11 p., https://doi.org/10.1016/j.scitotenv.2020.143387.

Zou, H., He, J.-t., He, B.-n., Lao, T.-y., Liu, F., and Guan, X.-y., 2019, Sensitivity assessment of denitrifying bacteria against typical antibiotics in groundwater: Environmental Science, Processes & Impacts, v. 21, no. 9, p. 1570–1579, https://doi.org/10.1039/C9EM00275H.

Knowledge Gaps and Opportunities in Water-Quality Drivers of Aquatic Ecosystem Health
Edited by Judson W. Harvey, Christopher H. Conaway, Mark M. Dornblaser, Allen C. Gellis, A. Robin Stewart, and Christopher T. Green
[Also see https://doi.org/10.3133/ofr20231085]

Chapter C

Anthropogenic and Geogenic Contaminant Bioexposures Affecting Aquatic Ecosystems

By A. Robin Stewart, Jeramy R. Jasmann, Elizabeth J. Tomaszewski, and Judson W. Harvey

Purpose and Scope

This chapter addresses knowledge gaps that, if filled, could improve predictions of aquatic ecosystem health as affected by anthropogenic and geogenic contaminant bioexposures. The gaps identified in this chapter are not intended to be comprehensive but are instead focused on key opportunities to fill those gaps for the U.S. Geological Survey (USGS) Water Resources Mission Area (WMA, https://www.usgs.gov/mission-areas/water-resources). Anthropogenic and geogenic contaminant effects on beneficial uses of water are not addressed in this chapter but are covered in Chapters C and D of Tesoriero and others (2024), the companion Open-File Report to this publication.

Statement of the Problem

Aquatic organisms are exposed to anthropogenic and geogenic contaminants (AGC) in water bodies via direct contact and (or) through diet, a process globally defined here as bioexposure. AGCs negatively affect aquatic ecosystems, including species diversity, and resiliency to water hazards (Chapman and others, 2010; Brack and others, 2019; Zhang and others, 2023). The economic effects of AGCs are significant due to the costs of restoration and mitigation of U.S. Environmental Protection Agency (EPA) Superfund sites, necessary infrastructure upgrades to wastewater and drinking water facilities, and loss of recreational and commercial fisheries (EPA, 2016, 2017, 2021a, 2021b). Furthermore, there are undesired consequences from water management projects (for example, water diversions) and habitat restoration where concentrations of AGCs may be altered, causing greater ecosystem harm (for example, wetland restoration enhancing mercury [Hg] methylation) (Chapman and others, 2010).

Water bodies where concentrations of some AGCs exceed established state water quality standards are listed under section 303(d) of the Clean Water Act (CWA; 33 U.S.C 1251 et seq.; https://www.epa.gov/tmdl), whereby States are required to rank and prioritize those waterbodies for the development of total maximum daily loads (TMDL). Following nutrients and sediments, AGCs such as Hg are listed as a primary cause of a water body being listed under the CWA. Yet, there are challenges associated with the CWA listing and the TMDL process. Federal and State water quality standards may not exist for AGCs detected in the water body, and for those that do have existing standards they may not be strict enough to protect aquatic life and resources. Quantifying AGCs in the environment is only the first step in establishing the significance of the detected AGCs and how they affect aquatic ecosystem health. Studying and understanding uptake mechanisms of AGCs is key to predicting contaminant fate and minimizing toxic effects. Reducing and mitigating AGC in water bodies is complex and requires detailed understanding of physical, chemical, and biological processes controlling the fate and effects of AGC loads entering ecosystems.

Regulators and resource managers require understanding and tools for: (1) attributing AGC loads to their sources, (2) quantifying AGC concentrations in space and time, (3) quantifying and incorporating direct and indirect factors (for example, biotic, abiotic) controlling bioexposure into coupled hydrologic-biogeochemical models, (4) linking bioexposures and effects, and (5) predicting changes in AGC fate in response to changing human and natural influences. Addressing these needs requires an approach that integrates investigation of physical and biogeochemical processes with data collection and model development.

While there are many key limitations in our understanding of mechanisms of anthropogenic and geogenic bioexposures and how they affect human and aquatic ecosystem health, the ecosystem health gap analysis team for the WMA Water Quality Program identified the following four major gaps grouped by anthropogenic or geogenic contaminant class (table C1):

- Anthropogenic contaminants of emerging concern (CECs)
    1. Major factors affecting human and aquatic organism health, and
    2. Water quality assessment tools for aquatic organism and human health risk.
- Geogenic contaminants
    1. Mechanistic understanding of uptake dynamics of geogenic contaminants for coupled hydrologic-biogeochemical watershed assessments and model development, and

Table C1. The four major bioexposure knowledge gaps of water quality drivers of aquatic ecosystem health identified by the U.S. Geological Survey (USGS), grouped by anthropogenic contaminants of emerging concern (CECs) or geogenic contaminant class.

[WWTP, wastewater treatment plant; LC50, 50 percent lethality concentration; BAC, bioaccumulation coefficients; BCF, bioconcentration factors; QSAR, quantitative structure-activity relationship; EPA, U.S. Environmental Protection Agency; K_d, distribution coefficient; DOM, dissolved organic matter; IWS; Integrated Water Science.]

What	Gap	Why	How	References
Anthropogenic Contaminants				
Major factors affecting human and aquatic organism health	Anthropogenic water use, specifically wastewater treatment plants (WWTP), which create complex mixtures of contaminants with unknown ecotoxicological effects.	WWTP discharge and toxicity benchmark data (that is, LC50, BAC, BCF) need to be consolidated in an accessible way to develop biogeochemical model parameters and improve understanding of bioexposure effects of complex mixtures of anthropogenic contaminants.	Laboratory-based aquatic organism feeding experiments in complex mixtures such as those in WWTP waters, along with in-situ mobile laboratory experiments to improve tools such as QSAR models.	Kolpin and others, 2002; Barnes and others, 2008; Focazio and others, 2008; Vajda and others, 2011; Bradley and others, 2016; Croteau and others, 2016.
Water quality assessment tools for aquatic organism and human health risk	Understanding of anthropogenic contaminant bioexposure and uptake is lacking and major improvements to databases and water quality tools are needed.	Predictive capabilities of anthropogenic contaminant bioavailability are limited. An ever-expanding list of contaminants and the complex biogeochemical processes at play need to be better accounted for in widely used models.	Compilation of an expanded database of contaminants of concern, in combination with laboratory and field studies to improve prediction capabilities. Development of screening tools including proxy measurements, computational toxicology tools and predictive modelling.	EPA, 2012, 2016, 2021a, 2021b; Faunce and others, 2023; Barber and others, 2022; Pavan and Worth, 2008a & 2008b; Ortiz de García and others, 2013; Omar and others, 2016; Fischer and others, 2017; Brack and others, 2019.
Geogenic Contaminants				
Mechanistic understanding of uptake dynamics of geogenic contaminants for coupled hydrologic-biogeochemical watershed assessments and model development	Methods to enhance understanding of factors and processes controlling uptake and bioavailability of geogenic contaminants for watershed assessments of risk and predictive modeling.	Partitioning of geogenics based on traditional assessments of total concentrations in water and particulate matter (that is, K_d) do not adequately assess risk at levels required by the regulatory community or numerically predict bioaccumulation in nature across a range of environmental conditions.	Field analysis of chemical speciation (that is, redox state, complexes), preservation, particle characteristics and hydrologic residence time along hydrologic-geochemical gradients coupled with chemical speciation modeling. Verify process controls on biouptake by laboratory feeding studies.	Luoma and Rainbow, 2009; Mebane and others, 2020; Ponton and others, 2020; Stewart and others, 1999; Croteau and others, 2005b & 2016. Nowell and others, 2014; Sangion and Gramatica, 2016.
Bioavailability and toxicity of organometallic complexes	Assess the bioavailability toxicity of metal-dissolved organic matter complexes, on a basin-by-basin case and incorporate results into more robust geochemical and ecotoxicological models.	Current models only account for total metal concentrations and the fraction that binds to biotic surfaces. Studies highlight that these complexes may be more bioavailable than believed and our understanding of metal uptake and toxicity needs updating.	A variety of in-situ and laboratory-based experiments to measure metal-DOM complex uptake and toxicity at the base of the food web (that is, microbes, algae). Experiments will vary with respect to metal, DOM source and biota based on IWS basin site specific needs.	Lamelas and others, 2005; Wang and others, 2019; Mebane and others, 2020; Stewart and Malley, 1999; Roditi and others, 2000; Sánchez-Marín and others, 2007; Parkhurst and Appelo, 2013.

2. Bioavailability and toxicity of organometallic complexes.

Status of Knowledge and Key Limitations

Broad factors that contribute to the bioexposure of AGC in aquatic ecosystems include sources and drivers, and mechanistic and biogeochemical processes (fig. C1). The introduction of AGC into aquatic ecosystems is influenced by contaminant sources (that is, urban land use, industrial, mining, and agricultural processes, and so forth) and drivers, such as extreme events related to climate change (that is, wildfires, droughts, and so forth) and land management practices (that is, wetland restoration, dams, irrigation, and so forth) (Kolpin and others, 2002; Barnes and others, 2008; Focazio and others, 2008; Bradley and others, 2016). These and other biogeochemical processes (that is, sorption, precipitation, speciation, redox changes, and so forth) determine loads, timing, and magnitude of concentrations of AGCs.

Within the receiving environment, ecosystem effects of AGCs are in part determined by mechanistic processes that influence contaminant transfer through the aquatic food web (fig. C1). Uptake from the dissolved phase into the base of the food web (that is, microorganisms, algae, detritus, sediment, and so forth) is influenced by (1) site-specific water quality (that is, temperature, dissolved oxygen [O], conductivity, oxidation-reduction potential, and turbidity), (2) concentration of the contaminant in the water column, and (3) physical and chemical properties of the contaminant that affect AGC transport, distribution and residence time within the hydrologic system, and (for metals) speciation. The capacity of a constituent to be taken up by a living organism and integrated into metabolic processes, or the fraction of the concentration that is absorbed and (or) adsorbed determines the "bioavailability" of a contaminant (de Paiva Magalhães and others, 2015). Certain AGCs that are consumed or absorbed by organisms that cannot catabolize or excrete quickly enough results in a buildup of the toxic chemical inside the organism, known as bioaccumulation. When the increasing concentration of a toxic chemical is transferred up the food chain, this process is known as biomagnification.

Contaminant transfer from the base of the food web occurs via the diet with trophic pathways playing an important role in determining bioexposures. Where an organism eats and diet composition can significantly alter bioexposures (Stewart and others, 2004), which highlights the important roles of ecology (Johnson and others, 2020), organism biology (Wang and others, 1996; Schlekat and others, 2002), and species invasions (Eagles-Smith and others, 2008; Lepak and others, 2009; Lepak and others, 2015) in providing an integrated assessment of contaminant

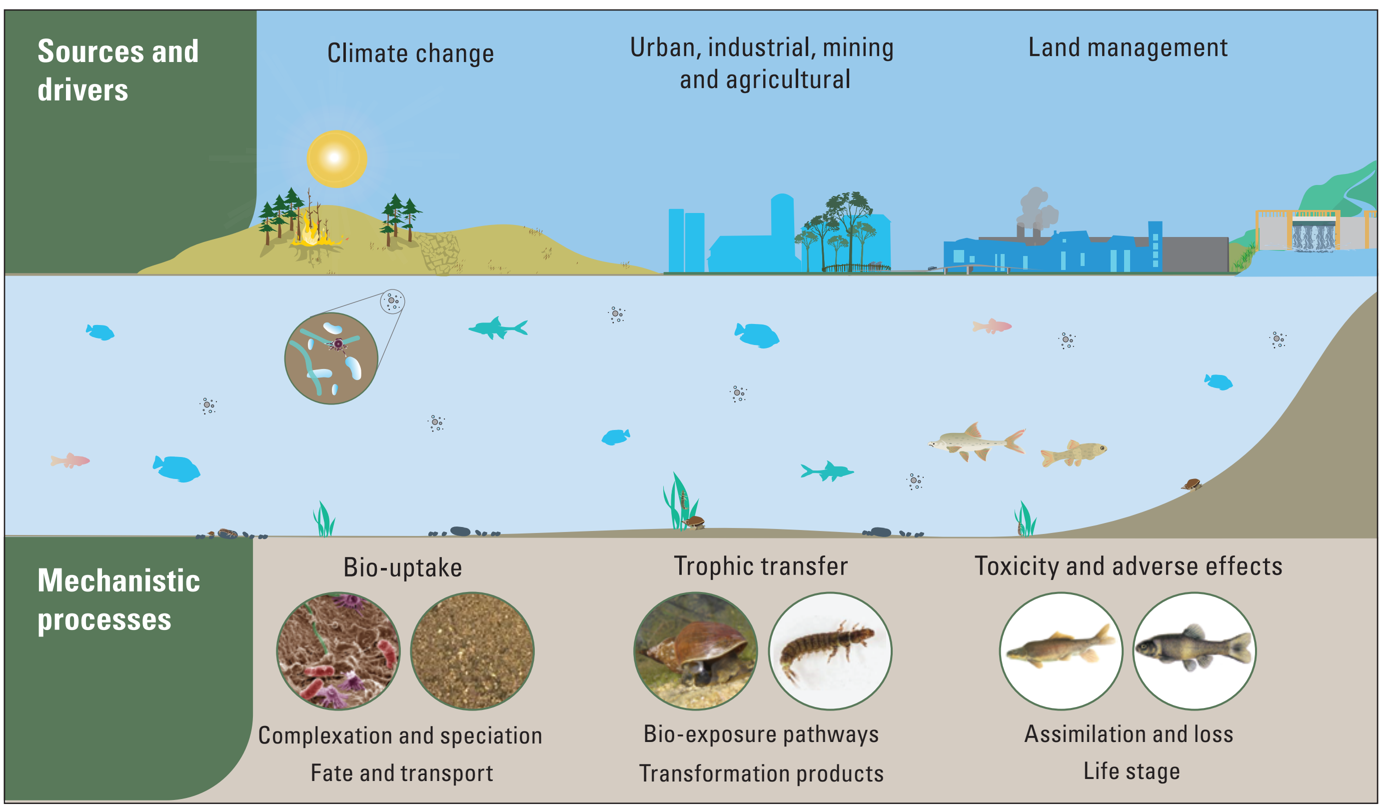


Figure C1. Drivers and mechanisms of bioexposure of contaminants in aqueous ecosystems illustrating different ways contaminants enter the food web and the factors influencing uptake and trophic transfer.

risk in watersheds. However, not all AGC bioexposures occur via the diet and for many classes of AGCs, the predominant uptake pathway is direct uptake from water (Griscom and others, 2000; Croteau and Luoma, 2005; Luoma and Rainbow, 2005; Vajda and others, 2011; Barber and others, 2012). However, due to many compounds included in the AGC classification and the individual chemistry these compounds possess, the relative importance of direct vs. dietary uptake for many AGCs is unknown or depends on the taxon.

Assimilated contaminants can interfere with fundamental biological processes, which then trigger toxic effects (Rainbow and Luoma, 2011). For example, the extent to which fish experience toxic effects depends on the duration of exposure, life stage of exposure (that is, maternal, larval, and so forth) (Johnson and others, 2020), whether a contaminant is assimilated or lost at this level of the food web, and interactions with other environmental stressors (that is, temperature, disease, food availability, and so forth).

These broad factors influence bioexposures of both anthropogenic and geogenic contaminants but the specific understanding and status of knowledge for these two contaminant classes can vary widely based on their chemistry and sources as discussed below.

Anthropogenic Contaminants

It has been well established that mixtures of anthropogenic chemicals are ubiquitous in urban streams and pose a potential threat to water quality (Kolpin and others, 2002; Focazio and others, 2008; Bradley and others, 2017; Bradley and others, 2018). The major drivers of increased future risks to aquatic organisms from AGCs include changes in regional climates (for example, more droughts and wildfires, loss of wetland habitats), changes in land-use needs (for example, urbanization, new crop production), and increasing human populations with increasing water use (Van Metre and others, 2019). There are research opportunities to develop or adopt water quality and toxicity screening tools for the prioritization of “at-risk” stream reaches or watersheds, and quantitatively link AGC concentrations to current effects, and model effects as a function of AGC use and concentrations (Fischer and others, 2017; Barber and others, 2019; Van Metre and others, 2019; Barber and others, 2022; Zhang and others, 2023). This can lead to better hydrologic model predictions and assessment tools for water resource managers to improve infrastructure and best practices to maintain water quality for many generations to come.

Anthropogenic organic chemicals that enter the aquatic environment through wastewater point-source and through non-point sources come in a wide variety of physicochemical properties. These chemicals have different controlling mechanisms for their environmental fate and transport and risks for toxicity or other adverse biological effects once they enter the aquatic environment or drinking water. Moreover, many organic chemicals are often purposely designed to be biologically active (for example, pharmaceuticals and pesticides), or disruptive to biological functions and cell membranes (for example, surfactants, disinfectants, peroxides), or resist biological degradation (for example, pharmaceuticals, per- and polyfluoroalkyl substances [PFAS], antioxidants, corrosion inhibitors). Some consumer, agricultural, and industrial products contain a mixture of chemicals having all these characteristics. The complexity of organic contaminants and aqueous mixtures is a challenge for summarizing collective effects on aquatic health. This challenge can be overcome by comprehensive site-based measurements of water chemistry and CECs and investigations of the exposure effects on the microbial and biological communities that exist and are exposed to this same complex mixture of chemicals (that is, simultaneous measurements and metrics). It is also important to fill in gaps in knowledge regarding bio-uptake rates and biomagnification of certain anthropogenic CECs. Moreover, strategic categorization of organic chemicals according to predominant sources or biological modes of action could promote faster assessment of overall risk and trend analyses to support decision making by water resource managers.

Geogenic Contaminants

Geogenic contaminants include metals (that is, cadmium [Cd], lead [Pb], Hg, zinc [Zn], manganese [Mn], chromium [Cr], and copper [Cu]) and metalloids (that is, arsenic [As], selenium [Se], antimony [Sb], and molybdenum [Mo]) that are concentrated and enriched in aquatic ecosystems by natural as well as anthropogenic activities that utilize geologic resources to meet core economic needs of society. Examples of such activities include the installation of drinking water wells, hard rock mining, oil refining, agricultural irrigation, and the construction of dams (Chapman and others, 2010). Wastewater discharge also contributes significant trace elements and metal contaminants into streams due to their use as purposeful constituents or impurities in consumer products (for example, Cr or cobalt [Co] in dyes, Zn or titanium [Ti] in sunscreens, As in household pesticides) or pharmaceuticals (for example, bismuth [Bi] in antibiotics, lithium [Li] in antidepressants). Drivers such as fire, climate (that is, precipitation), and hazards (that is, flooding), along with disturbance from human activities further enhance weathering and mobilization of geogenic contaminants from the landscape and delivery via dissolved and particulate forms to aquatic environments.

While TMDLs are focused on loads, those loads need to be converted into concentrations because bioavailability and toxicity effects to aquatic organisms are related to concentration. Indeed, EPA criteria are most often in the form of concentrations for which toxicity benchmarks and thresholds are based. Metal and metalloid bioexposure to aquatic organisms has been described by total concentrations (that is, the sum of all chemical species) or using thermodynamic models such as the free ion activity model (FIAM) and (or) the biotic ligand model (BLM). Both models assume the only bioavailable form of metals is the aqueous free ion, assuming direct and linear relationships between free ions and biological surface-bound metal species (Zhao and others, 2016; Mebane and others, 2020). However, these models do not account for uptake and exposure pathways beyond direct uptake of metal ions and biotic ligand complexation.

Total water column concentrations of geogenic contaminants alone are rarely reliable predictors of bioexposure, toxicity risk, and ecosystem health. Chemical speciation is an important factor when considering toxicity, bioavailability, and bioaccumulation across food webs. According to the International Union of Pure and Applied Chemistry (IUPAC) definition, chemical speciation refers to a specific form of an element defined as to isotopic composition, electronic or oxidations state, and (or) complex or molecular structure. By this definition, several changes in speciation can occur in the water column. For example, seasonal changes in dissolved O concentrations can not only induce oxidation state changes in geogenic contaminants but also changes in dissolved organic carbon (DOC) speciation and subsequent interactions with metals and biota. Transition metal (iron [Fe] and Mn) (oxyhydr)oxides and oxides can undergo reductive dissolution in anoxic environments, leading to the release of adsorbed metals and metalloids. Geogenic contaminants such as Cr, Hg, As, Se, and Sb can all be present with multiple oxidation states in aquatic environments and usually have a particular oxidation state that is more bioavailable and toxic compared to others. For example, As(III) is more toxic compared to As(V) (Spehar and others, 1980), but the opposite is true of Cr. In its reduced state, Cr(III) is generally less soluble and less toxic compared to the oxidized state Cr(VI) (Velma and others, 2009). Beyond changes in oxidation state, redox conditions also influence biological activity that can alter metal toxicity. For example, under anoxic conditions, As and Hg can undergo metabolic processes that produce toxic, methylated species, the latter of which bioaccumulates strongly across food webs (Brigham and others, 2009; Selin, 2009). Other metal C species that may form depending on redox conditions are organometallic complexes (Velma and others, 2009). Dissolved organic carbon speciation and metal complexing capacity are correlated in part to redox conditions, in that the abundance and quality of C will be altered depending on biological activity. The toxicity and bioavailability of these metal-carbon complexes are poorly understood.

Dissolved inorganic contaminants can also change from aqueous to solid species because of the precipitation of mineral phases. Chalcophilic metals and metalloids such as Hg, Zn, Pb, As and Cd can precipitate as sulfidic phases in the environment, especially under reducing conditions. Precipitation of these phases can radically decrease bioavailability and potential for bioaccumulation across food webs; however, if shifts in geochemical conditions occur, dissolution of the phases may lead to renewed bioavailability.

Physical and chemo-physical processes can also influence contaminant speciation and partitioning on to particles. Processes such as perturbation from benthic invertebrates or turbulence and scouring during high flow events can lead to higher concentrations of particulate matter in the water column that can adsorb geogenic contaminants. Particulate-adsorbed geogenic contaminants can have multiple effects on bioexposures. They can result in contaminant sequestration, if the complex is not biologically available, enhanced uptake via dietary consumption, transport, or burial via sedimentation processes. Yet, these processes also depend on the characteristics of the particles present in the environment, including grain size and organic content, which can vary significantly in space and time ((Brigham and others, 2009; Stewart and others, 2008).

Whether a geogenic substance is an essential element further influences bioexposure. In the case of metal cation contaminants, microorganisms generally exhibit two primary water uptake mechanisms: (1) nonspecific binding to cell surfaces and biomass, and (2) metabolism-dependent intracellular uptake (Gadd and Griffiths, 1977; Stewart and others, 2010). Adsorption of metal cations to biomass is far more common, as metabolism-dependent intracellular transport is not only an energetically costly process but also can lead to the precipitation of intracellular metal phases, requiring the expression of tolerance mechanisms (Gadd and Griffiths, 1977). Uptake of the essential element Se, which forms oxyanions in the aqueous environment, is predominantly through an energy-mediated process (Stewart and others, 2004, 2010). For this reason, the partitioning of Se on inorganic particles in sediments tends to be low relative to its absorption by algae, making particle characterization necessary when trying to discern differences in Se associated with the particulate fraction both within and among aquatic systems (Ponton and others, 2020).

Trophic transfer of geogenic contaminants is highly dependent on trophic-specific and species-specific assimilation and loss (Reinfelder and others, 1998). For example, methylmercury (MeHg) is biomagnified in food webs because the proportion of MeHg to inorganic Hg increases with each trophic level and the loss of MeHg by an organism is relatively slow (Lavoie and others, 2013). Alternatively, studies have shown that Cd is biomagnified within distinct invertebrate and fish food webs, with invertebrate food webs having higher trophic enrichment factors than fish food webs (Croteau and others, 2005). In the case of Se, large differences in Se uptake have been quantified among algal and invertebrate taxa resulting in corresponding large differences along trophic pathways in Se concentrations in consumers and predators (Baines and Fisher, 2001; Stewart and others, 2004).

Priority Gaps in Anthropogenic and Geogenic Bioexposures

Table C1 presents a summary of the bioexposure knowledge gap analysis for ecosystem health and function. More details about these knowledge gaps and approaches to fill the gaps are presented in this section.

Anthropogenic Wastewater Contaminants of Emerging Concern Gaps

In a recent synthesis paper by Abbott and others (2019) comparing 464 water-cycle diagrams from around the world, it was estimated that approximately 24,000 cubic kilometers per year ($km^3 \cdot yr^{-1}$) is now used for human freshwater appropriation for livestock, croplands, forestry, industrial and domestic water use, and water necessary to dilute human pollutants (wastewater use). This human use redistributes the equivalent of half of the global river streamflow and double the global groundwater recharge each year (Abbott and others, 2019). Despite this fact, it was determined that only 15 percent of the water-cycle diagrams represented human interaction with the water cycle, and only 2 percent showed climate change or water pollution effects on the water availability and quality. This is an important gap in water budget and water quality modeling and the USGS is well equipped to improve assessments of water security and sustainability by integrating human water use and indirect reuse into our hydrologic models. Human water use, reuse, and returned flows have become a major component of the global water cycle, resulting in significant contributions of additional nutrients, salinity shifts, and complex mixtures of CECs added to our Nation's surface water and groundwater (Kolpin and others, 2002; Abbott and others, 2019; Bradley and others, 2017, 2018; Barber and others, 2019, 2022). Treated domestic and industrial wastewater discharge, agricultural/irrigation and urban stormwater return flows, and chemical spills are all large contributors of these complex mixtures of CECs along with their associated adverse effects on water quality and ecosystem health downstream (Kolpin and others, 2002; Barber, 2014; Bradley and others, 2016; Fischer and others, 2017; Croteau and others, 2005, 2016; Masoner and others, 2019; Battaglin and others, 2020). With increasing and ever-changing mixtures of CECs being added to the natural aqueous environment through wastewater return flows, it is imperative for humans to better understand the adverse effects on human and ecosystem health and recreational sustainability, including the major drivers of these bioexposures and sources of priority pollutants.

Gap 1. Major Factors Affecting Human and Aquatic Organism Health

Wastewater Discharge and Toxicity Benchmark Data

At present there is no consolidated database of contaminant loads from the wide range of wastewater effluents discharged to natural waters. The scientific literature has many studies that investigate CECs detected in municipal WWTP effluent and sludge. This is largely facilitated by the fact that most municipal WWTP facilities are publicly owned treatment works (POTWs) and have publicly accessible information available through discharge permits. Some of these data for major point source discharges, including WWTPs, can be found using EPA's Enforcement and Compliance History Online (ECHO) tool (https://echo.epa.gov/) and EPA's Clean Watersheds Needs Survey (CWNS, https://www.epa.gov/cwns). However, other sources are often needed to obtain the treatment type and population served by the WWTPs, which allows for better fitting of chemical loads per capita and per treatment type to be used in modeling new watersheds. Other wastewater return-flow data are more difficult to obtain, such as those from industrial WWTP and mining discharges, as well as from non-point sources like agriculture or urban stormwater.

It is also difficult to obtain a consistent data set of aquatic toxicity benchmarks such as predicted no effect concentrations (PNECs), effect concentration at which 10 percent of a population is biologically affected (EC10), CMCs, or 50 percent lethality concentration (LC50) for the multitude organic contaminants used for pesticides, industrial applications, pharmaceuticals, or consumer products that are released into the aquatic environment (Brack and others, 2019). Similarly, a major data gap exists for bioaccumulation coefficients (BACs) or bioconcentration factors (BCFs) for priority pollutants; having this would help to better asses the health risk to aquatic organisms at different trophic levels, and potential risk to predator terrestrial organisms (including humans) that feed on aquatic organisms. Moreover, organic contaminants with high octanol-water coefficients (K_{ow}) can be an important driver to better understand which chemicals will bioaccumulate in fatty organs of the body like the liver or brain. Efforts to calculate, validate, or consolidate these BACs, BCFs, and toxicity benchmarks could form the basis for guidance documents on acceptable aqueous concentrations of CECs for different water use expectations. A collaborative effort by the USGS and other Federal agencies could provide the evidence-based scientific support and relevant toxicity benchmarks to stand up TMDLs for CECs currently lacking Federal regulation. USGS has particular expertise in addressing potential adverse biological effects caused by bioexposure of organisms to chemical loads associated with wastewater reuse.

Biogeochemical Model Parameters

Process-based models are only reliable with sufficient data for estimating parameters that will constrain the model simulations to perform accurate predictions. To be able to couple hydrologic and reactive transport models with ecological risk models, a deeper understanding of many of the biogeochemical processes in complex aqueous mixtures is needed to parameterize the models. Some essential parameters include chemical solubility, partition coefficients, complexing capabilities, and chemical degradation rates from biological or physical transformations in natural streams and WWTPs. The USGS is well-positioned to carry out laboratory-based and field-based investigations to identify processes controlling the transport and fate of anthropogenic organic contaminants in the aquatic environment, along with the possible exposure pathways to aquatic organisms and humans. Examples of existing USGS Water Mission Area (WMA) capabilities that could be expanded upon include: (1) laboratory exposure of aquatic snails to uranium (Croteau and others, 2016) and other contaminants of concern in the presence of different water chemistry conditions, and (2) continuous-flow mobile laboratories located on-site to test the endocrine or toxicity effects of wastewater effluent or agriculture runoff on fat head minnows (*Pimephales promelas*) (Barber and others, 2012, 2013, 2019) or other organisms in stream environments.

Gap 2. Water Quality Assessment Tools for Aquatic Organism and Human Health Risk

Water resource managers need better water quality assessment tools to sustain healthy streams and drinking water sources (Fischer and others, 2017). These tools include more affordable analytical measurements for CECs, access to CEC experts to assist with data interpretation, and production of hydrologic models that can simulate and predict stream concentrations of CECs in relationship to toxicity tolerance levels in a variety of climatic and water management scenarios. Owing to the variety of organic anthropogenic chemicals and the lack of sufficient empirical data for all their physicochemical properties and aquatic toxicology benchmarks, computation models could be used to supplement some of the information. These quantitative structure-activity relationship (QSAR) models use common molecular structures to estimate unknown physicochemical parameters to derive environmental fate, biodegradability, and potential toxicity tolerances of various organism types, are discussed in more detail in the “Develop Tools for Screening-Level Contaminant of Emerging Concern (CEC) Assessments” section.

Sustaining a healthy aquatic ecosystem for aquatic organisms, drinking water, and recreational use depends upon both water availability and water quality and requires scientifically informed water management decisions. Sufficient flow volumes are needed throughout the year by critical aquatic species to provide appropriate habitat space, aerated mixing, and maintain cool enough water temperatures. Water quality changes caused by anthropogenic activities and land use are also dominant drivers controlling the complex chemical mixtures that aquatic organisms are exposed to in streams, rivers, and lakes.

Bioactive anthropogenic chemicals released to the environment through spills and wastewater discharge pose direct toxicological and endocrine disruption risks to aquatic organisms (Omar and others, 2016). There are thousands of bioactive chemicals released into the aquatic environment from different product applications with a wide range of physicochemical parameters and ecotoxicology profiles (Kolpin and other, 2002). Water resource managers and regulators will continue to need scientific studies and new data to develop new tools and approaches for monitoring and modeling chemical concentrations, investigate mechanistic processes controlling fate and bio-exposure pathways of CECs, and provide interpretions to support water resource management decisions (Fischer and others, 2017). Filling these gaps will allow for the integration of chemical loading from major point-sources and non-point sources of anthropogenic return flows into the next generation of USGS water budget and reactive transport models to gain a more accurate water quality representation of our United States freshwater resources.

Develop Risk Prioritization Scheme

Water resource managers and citizens needing clean drinking water and desiring safe recreational opportunities can benefit from consistent, easy-to-use tools that assess the relative risks and management opportunities for CECs in the Nation’s waters. Prioritization of the abundance of thousands of aquatic CECs with wide ranging sources, chemical classes, fate-controlling processes, and risk concerns makes it extremely challenging to carry out comprehensive and ongoing monitoring. To close this gap, the USGS could develop or adopt a consistent, evidence-based schema for prioritization of at-risk watersheds and high priority anthropogenic and geogenic CECs at the national and regional scale for different geographical and hydrological watershed types. There are existing risk prioritization schemes from USGS and others looking at stream concentrations in relationship to PNECs; persistence, bioaccumulation, toxicity, environmental occurrence (PBTO indices); regulatory pressure; risk perception by the public; along with other risk criteria and decision support systems that can be adapted to meet USGS stakeholder needs (Ankley and others, 2010; Ortiz de García and others, 2013; Nowell and others, 2014; Ortiz de García and others, 2014; Gramatica and others, 2016; Sangion and Gramatica, 2016; Card and others, 2017; Fischer and others, 2017; Covert and others, 2020; Medlock Kakaley and others, 2020; Barber and others, 2022; Faunce and others, 2023).

There are also publicly available databases that can be used to assist with compiling some of the data needed, including the EPA’s Estimation Parameter Interface (EPI) Suite (EPA, 2012; Card and others, 2017) and CompTox chemical dashboard (EPA, 2016a), the Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides (EPA, 2021a), PubChem database (Kim and others, 2020), and PPDB—Pesticide Properties databases (Agriculture & Environment Research Unit [AERU], 2021). In addition, the EPA maintains a database of registered pesticides that have documented acute (that is, lethal concentration to kill 50 percent of a population [LC50] and half maximal efficiency concentration [EC50]) and chronic aquatic life benchmarks (ALBs) in fish, invertebrates, and aquatic plants (EPA, 2021a). It is much more difficult to find empirical measurements in the literature of these ALBs for non-pesticide CECs. The EPA has also established national recommendations for aquatic life criteria (criterion maximum concentrations [CMCs] and criterion continuous concentrations [CCCs]) for around 60 organic and inorganic toxic chemicals (EPA, 2021b). However, this list is mainly limited to nationally regulated chemicals and lacks criterion for thousands of other toxic and bioactive chemicals that need to have toxicological endpoints determined. The USGS could help fill this data gap by conducting a systematic collection and common databasing of toxicity endpoint criteria for aquatic organisms (for example, PNEC, environmental quality standard [EQS], no observed effect concentration [NOEC], lowest observed effect concentration [LOEC], EC50, LC50, and so forth) for a prioritized list of chemicals analogous to comprehensive aquatic toxicity databases (Norman and others, 2018) and tables in supporting information of Barber and others (2022). Examples include EPA’s maximum contaminant levels [MCLs] (https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations), EPA Human Health Benchmarks for Pesticides (https://www.epa.gov/sdwa/2021-human-health-benchmarks-pesticides), and

USGS Health-Based Screening Levels (https://www.usgs.gov/programs/environmental-health-program/science/usgs-health-based-screening-levels-available-online), along with a method for normalizing these criteria to allow cross comparisons for hazardous rankings (Norman and others, 2018). A similar open-access database could address physicochemical and biological uptake properties as well, starting with curating empirical data from the literature and credible databases.

Develop Tools for Screening-Level Contaminant of Emerging Concern Assessments

The development of (1) proxy-chemical analyses, (2) assimilation of computational toxicology and (3) predictive modeling for CECs would allow the USGS to provide screening-level assessments to support water resource decisions and to guide future monitoring and research studies in Next Generation Water Observing Systems (NGWOS) and IWS basins.

8. Proxy-chemical analyses: Spending time and resources to develop rapid, screening-level analytical methods that analyze for surrogate chemicals and metabolites across a range of chemical classes or source types could save money on costly analysis of larger suites of chemicals until after "contaminant hot spots" are identified. To make this analysis rapid and cost-effective, it cannot be all-inclusive and so finding suitable surrogate chemicals for entire chemical classes/source types and (or) other chemical proxies will be necessary. The combined scientific expertise of the USGS along with nation-wide access to NGWOS and IWS water basins allows for the USGS to use an "Integrated Design Approach" to investigate prioritized CEC effects and controlling processes. The ideal approach is to integrate multiple disciplines (for example, organic geochemists, hydrologists, biologists, and modelers) into NGWOS and IWS basin studies from the beginning.

9. Assimilation of computational toxicology: Due to the lack of empirical data for environmental fate parameters, biological uptake mechanisms, and toxicity endpoint criteria for the thousands of chemicals released from pharmaceuticals, consumer products, urban homes, and transportation systems into the environment, computational tools are an efficient way to screen large sets of chemicals in a short time with the potential for ranking the most environmentally hazardous constituents. The computational tools applied to organic chemical contaminants often rely on QSAR models. These are regression models that use structural molecular descriptors within organic chemicals and commonly measured fate parameters like water solubility and octanol/water partition coefficient (K_{ow}) to predict environmental fate parameters and biological activity of chemicals with similar descriptors. For example, the K_{ow} is important for assessing organic contaminant fate and transport, because hydrophobic compounds (log K_{ow}>3) preferentially accumulate in solid phases and hydrophilic compounds (log K_{ow}<3) preferentially occur in the aqueous phase. QSAR tools like those found in EPA's EPI Suite interface are being used to help make predictions of environmental concentrations of CECs and produce hazardous ranking indexes like (i) $PNEC_{equivalents}$ and Risk Quotients (Barber and others, 2022; Faunce and others, 2023), (ii) apply PBTO indices to rank persistence, bioaccumulation, toxicity, and environmental occurrence (Ortiz de García and others, 2013; Sangion and Gramatica, 2016), or (iii) provide a software tool for Decision Analysis by Ranking Techniques (DART; Pavan and Worth, 2008a & 2008b) to support the ranking of chemical according to their environmental and toxicological concern.

10. Predictive modeling for CECs: The USGS accumulated wastewater ratio (ACCWW) on-line mapper is a versatile tool which can combine empirical data inputs (when available) with QSAR-based inputs (EPA, 2012 & 2016) coupled with streamflow, wastewater discharge, and ecotoxicity models to produce geographic information system (GIS) maps of watersheds and stream reaches showing predicted environmental concentrations of CECs (Kandel and others, 2017; Faunce and others, 2023; Barber and others, 2022). This provides a powerful screening-level assessment tool for regional watersheds that can be scaled up to national level or scaled down to local level. Innovative platforms for presenting water availability, water quality, and water suitability on GIS maps can improve the speed and accessibility of science data delivered. The supporting information of Barber and others (2022) provides a large data table of pharmaceuticals, personal care products (PPCP), and pesticides ecotoxicity benchmarks (LC50, EC50, PNECs, NOECs) from literature-based empirical data and EPI Suite ECOSAR model predictions, and also includes an accumulated wastewater model for the Shenandoah watershed with a risk prioritization scheme using water quality data.

Geogenic Contaminant Gaps

Gap 3. Mechanistic Understanding of Uptake Dynamics of Geogenic Contaminants for Watershed Assessments of Risk and Coupled Hydrologic-Biogeochemical Model Development

A key gap in understanding how geogenic contaminants result in bioexposures that affect ecosystem health are the factors and drivers that control the availability of geogenic contaminants in water and particulate material (Luomo and Rainbow, 2009). Specifically, what environmental conditions favor dissolved chemical species of metals that are readily adsorbed onto particles or directly taken up by microorganisms, algae, or plants? Then, once associated with particles (sediments or organic material), what types of particles favor high assimilation of metals by aquatic species? Given that many metals, including metalloids, like As and Se, show the largest enrichment at the base of aquatic food webs, from water onto particles, understanding of these fundamental processes could lead to significant improvements in evaluating bioexposures as part of integrated assessments (Stewart and others, 2010).

The complexity of resolving these processes across systems can be daunting. In the absence of a more mechanistic approach, scientists have utilized distribution coefficients (K_d), a ratio that quantifies the partitioning of dissolved forms of metals onto particles. The K_d ratio is defined by the concentration of the constituent in particulate phase divided by the concentration in water. Over the past several decades this ratio has been used to evaluate bioavailability of mined metals (Stewart and Malley, 1999) and extensively in the "Ecosystem Selenium Model" developed by Presser and Luoma (2010) and for developing EPA site-specific criteria for Se. In the case of Se, partitioning inferred from K_d values was found to vary over several orders of magnitude among systems (freshwater to marine), which could be attributed in part to Se species (that is, selenate, selenite, selenomethonine), residence times, and particle types (that is, sediment, biofilms, filamentous algae) (Presser and Luoma, 2010). While K_d ratios for Se may be effective in identifying and even predicting gross differences in partition of Se among systems, they often lack the resolution within watersheds to estimate differences in bioavailable Se at spatially and temporally relevant scales. Moreover, without the mechanistic basis underlying the differences in K_d, it is not possible for resource managers to identify specific factors controlling bioexposures in food webs for the development of mitigation strategies. Mechanistic processes are also required for building coupled hydrologic-biogeochemical models for anticipating changes in bioavailable Se and other metalloids and metals in response to climate and resource management actions. A mechanistic approach to assessing and predicting changes in geogenic bioexposures would include understanding: (1) biogeochemical (that is, redox, pH, DOC, sulfate, and so forth) and hydrologic (that is, mixing, residence time) controls on chemical speciation, (2) potential for different chemical species to be adsorbed and (or) accumulated by different particles (that is, sediment, microorganisms, algae, and plants), and (3) relative assimilation of aqueous versus particulate chemical species by organisms. Given their inter-dependent nature, these processes could be evaluated jointly to determine their net effect in different aquatic environments.

The USGS can investigate these processes across a range of geochemical and hydrological conditions, for example, initially in relevant IWS basins such as the Upper Colorado River as well as other basins with outstanding Se and related metal or metalloid problems such as the Kootenai River (Idaho and Montana). Selenium and other geogenic metalloids and metals derived from mining remain a concern for resource managers in these areas (EPA, 2017) and there are ongoing research efforts (such as transboundary projects) that could provide historical and ongoing data collections to support the process research (Chapman and others, 2010). This effort could later be extended to the other IWS basins (that is, the Delaware River and Illinois River Basins) as appropriate to validate processes and model applications.

Biogeochemical Controls on Chemical Speciation

This approach uses field based water quality collections of total and dissolved geogenic species and ancillary parameters (that is, redox, pH, DOC, sulfate, nutrients, suspended solids, and so forth) combined with speciation modeling (Visual Minteq, https://vminteq.lwr.kth.se/; and PHREEQC, https://www.usgs.gov/software/phreeqc-version-3) (Parkhurst and Appelo, 2013). The goal is to determine how measured chemical speciation changes with geochemical conditions and test if those changes can be estimated using geochemical speciation models. Speciation can be defined as oxidation state, phase change (for example, adsorption to particulate matter, precipitation as a solid) and complexation with dissolved organic compounds. Sites could be chosen along geochemical gradients and hydrologic residence times. Geogenic elements could be selected for this work based on WMA, Federal partners, state agencies, and stakeholder priorities.

Chemical Speciation Controls on Particulate Adsorption and Bioaccumulation

This approach determines how chemical species (quantified above) are adsorbed or accumulated by different particle types that can influence their bioavailability. Quantifying particle characteristics in nature and corresponding aqueous geochemical conditions can enhance understanding of the controls that particles exert on metal speciation. This entails characterization of particulate material and geogenic particulate concentrations from sites described previously. Particulate material (greater than 0.45 micrometer [µm]) will be characterized by: (1) physical characteristics (that is, particle size and concentration), (2) inorganic composition (that is, grain size, Fe, Si, aluminum [Al] content, and so forth), (3) organic matter content and composition (that is, percent carbon, chlorophyll a, stable isotopes $\delta^{13}C$, nitrogen-15 [$\delta^{15}N$], and sulfur-34 [$\delta^{34}S$] signatures), and (4) algal and biomass taxonomy. Chemical extractions, specific elemental analysis (CHNS analyzer), TOC analysis and stable isotope analysis are all example of initial characterization techniques. Flow fractionation inductively coupled plasma mass-spectrometry (ICP-MS) and spectrometric methods offer other analytical approaches for particulate matter characterization. Additionally, particle-bound metal speciation (for example, oxidation state, organo-metallic complexes, and so forth) can be characterized using advanced spectroscopic techniques such as X-ray adsorption spectroscopy (XAS). This technique will help answer mechanistic questions about metal speciation and associations with elements such as Fe and Al in particulates. The information can then be used to improve predictive geochemical models, better accounting for speciation and the influence of particulate matter on bioavailability. The knowledge of this technique resides within the Strategic Laboratory Science Branch (SLSB) of Laboratory and Analytical Services Division (LASD) in WMA. Typically, this technique is carried out at a synchrotron facility and the idea is that these measurements will be paired with in-house techniques (that is, chemical extraction, Fourier

Transform infrared spectroscopy, and so forth) to create a framework of understanding. However, benchtop XAS is possible and could be explored in the future.

Assimilation of Geogenic Contaminants from Inorganic and Organic Particles

This approach combines field assessments of dissolved chemical species and particulates and to determine their control on bioavailability to biota (that is, invertebrates or fish). Results from field measurements could be used to guide laboratory uptake experiments in the form of feeding studies. The feeding studies could utilize different particle and dissolved metal species, using well proven methods (Cain and others, 2016; Croteau and others, 2017).

Hydrologic Controls on Chemical Speciation and Particulate Bioavailability

Hydrological investigations can provide insight into how transport processes that affect residence times influence biogeochemical transformation and speciation, geogenic adsorption and bioaccumulation. Residence times can be estimated at field sites to aid in the evaluation of differences in bio-uptake among data from different locations.

Gap 4. Bioavailability and Toxicity of Organometallic Complexes

Another geogenic gap is bioavailability and toxicity of organometallic complexes. Models such as FIAM and BLM often underestimate metal and (or) metalloid bioexposure, not accounting for the bioavailability of organometallic complexes (Mebane and others, 2020). Natural dissolved organic matter (herein identified as DOM) is an example of a widespread environmental metal or metalloid complexing agent whose reactivity is overlooked by these classic thermodynamic models. DOM has varying degrees of reactivity toward metal/metalloids depending on chemical properties, such as molecular weight, chemical structure, and functionality (Cory and McKnight, 2005), and environmental properties such as DOM source and geochemical conditions (for example, pH, ionic strength, and redox conditions). For example, calcophile metals such as Cd, Pb, Hg, and Zn all bind strongly to thiol groups associated with DOM (Shindo and Brown, 1965; Chen and others, 2017; Lescord and others, 2018). Similarly, sulfidic groups associated with DOM have been shown to be important complexing agents of arsenite (Hoffman and others, 2013). However, changes in metal oxidation state as well as changes in DOM acidity and functionality influence metal complexation (Ren and others, 2017). Thus, predicting metal complexation with DOM is not always as simple as a straightforward calculation.

As complicated as the formation of metal- or metalloid-DOM complexes is, understanding the influence on bioavailability and uptake of these complexes adds another layer of complexity. The specific metal or metalloid, the type and chemical characteristics of DOM and the organism all influence organometallic complex uptake and bioaccumulation across food webs. For example, Cd-uptake rates in Zebra mussels (*Dreissena polymorpha*) were 52–61 percent lower when complexed to humic acid (HA, a fraction of DOM) compared to the free ion but still higher than predicted by FIAM, with some Cd-HA accumulation in the organism (Voets and other, 2004). A study with zebra mussels demonstrated different extents of uptake of Cd, silver (Ag), and Hg depending on whether low molecular-weight or high molecular-weight DOM was present (Roditi and others, 2000). In the presence of HA, fulvic acid (FA) and different polysaccharides, the uptake of Pb by green algae was less than the free ion (Pb^{2+}) but still greater than FIAM-predicted values (Lamelas and others, 2005). Complexation with HA and FA lead to higher internalized concentrations of Pb compared to polysaccharides, demonstrating how the type of OC can influence the extent of uptake (Lamelas and otheres, 2005). A study in artificial sea water showed that Pb uptake and toxicity in marine invertebrates—blue mussels (*Mytilus edulis*) and sea urchins (*Paracentrotus lividus*)—actually increased when complexed with HA compared to the free Pb ion (Sánchez-Marín and others, 2007). The bioaccumulation of Cu also has been shown to increase in algae when high initial Cu concentrations are complexed with low molecular-weight FAs (Shi and others, 2018). Higher molecular-weight FAs have been shown to contain more aliphatic functional groups and less carboxyl groups per unit C mass (Tan and Giddens, 1972; Reemtsma and These, 2005; Shi and others, 2018), which makes it less susceptible for binding with cationic metals such as Cu.

The source of DOM affects molecular composition, affecting reactivity with metal or metalloids and subsequent complex bioavailability. DOM can be autochthonous, meaning it is derived from an aquatic ecosystem (that is, detritus, biomass, and so forth) or allochthonous, meaning it is terrestrially derived (that is, plants, soil, and so forth). Allochthonous DOM is generally considered more recalcitrant compared to autochthonous DOM, as heterotrophic and autotrophic metabolic processes generally lead to the production of small aliphatic acids, while plant and soil organic matter can be more aromatic and thus, typically considered less biodegradable (Thurman, 1985). Molecular composition of DOM varies spatially and temporally due to its proximity to source material and its exposure to environmental processes such as biodegradation and photodegradation (Helms and others, 2008; Hansen and others, 2016). DOM composition can also be influenced by anthropogenic activities. For example, DOM composition along a WWTP-river-lake continuum was shown to vary greatly, with the ratio of protein-like to humic-like carbon notably decreasing and the percentage of humic-like carbon increasing (EPA, 1999; Barber and others, 2001; Wang and others, 2019). Therefore, when considering the bioavailability of organometallic complexes, it is important to consider changes in DOM composition that may occur in the environment and how this could influence the extent of metal or metalloid complexation.

Bioexposure Studies of Metal-Dissolved Organic Matter Complexes with Organisms at the Base of the Food Web

This approach could involve field and laboratory-based experiments, which will lead to the development of analytical tools and the improvement of existing bioexposure models.

Experiments could vary with respect to four factors: (1) metal and (or) metalloids of interest, (2) DOM characteristics sources, (3) microbial species, and (4) analytical techniques. We suggest beginning studies by focusing on microbial species, as they are a key component of the base of the food web; however, there are many data gaps that exist for other aquatic species such as invertebrates. The intention is that studies could build in complexity, both from a geochemical and ecological standpoint.

Metal or metalloids of interest could be prioritized based on the needs of IWS such as the Upper Colorado, Delaware, and Illinois River Basins. This determination will involve reconnaissance of IWS basin aqueous geochemical conditions via field campaigns and analysis of available historical data. Field and lab measurements, as well as historical data, could be incorporated into speciation models, such as PHREEQC, to confirm and predict dominant metal or metalloid species, as discussed in the "Biochemical Controls on Chemical Speciation" section in this chapter.

During experiments, DOM from different sources with different chemical characteristics could be varied to evaluate differences in metal-DOM binding and effects on bioexposure. Sources of DOM will vary by basin environments and by environments affected by anthropogenic activity (that is, WWTP, urban, agricultural). Constraints could be imposed based on the importance or contribution to an environment of interest.

Microbial species are an essential part of the base of the food web composition and as such it is important to specifically understand the bio-exposure of metal-DOM complexes to these species. Beginning work could focus on microbial species to establish an understanding at the base of the food web and future studies could examine bioavailability to more complex organisms. Both pure culture and whole community experiments could be conducted in the laboratory. Cell numbers, growth rates and potentially genes of interest could be quantified in relation to metal-DOM complex exposure.

Laboratory-based experiments could be designed to measure metal-DOM complexes in new and novel ways. Ideal DOM sources such as Suwannee River fulvic acid could be used with metals to prepare metal-DOM complexes and chromatographic and spectroscopic techniques could be explored for detection and quantification of organometallic complexes.

Timelines

Table C2 presents a suggested timeline to conduct prioritized USGS approaches for closing knowledge gaps to address the anthropogenic and geogenic contaminant bioexposures affecting aquatic ecosystems outlined in this chapter.

Table C2. Timeline summary of prioritized U.S. Geological Survey (USGS) approaches to closing knowledge gaps for the anthropogenic and geogenic contaminant bioexposures affecting aquatic ecosystems.

[DNA, deoxyribonucleic acid; K_{oc}, carbon-water coefficient; K_{ow}, octanol-water coefficient; yr, year; IWS, Integrated Water Science; PNEC, predicted no-effect concentrations; EC50, half maximal efficiency concentration; CEC, contaminant of emerging concern; WWTP, wastewater treatment plant; QSAR, quantitative structure-activity relationship; DART, decision analysis by ranking techniques; GIS, geographic information system.]

Advancements	Major processes affecting human and aquatic organism health	Water quality assessment tools for aquatic organism and human health risk implications	Mechanistic understanding of uptake dynamics of geogenic contaminants	Bioavailability and toxicity of organometallic complexes
Near-term (2-yr)	Organization and access to data for assessing indirect water reuse affecting biota. Focusing on physicochemical properties such as water solubility, K_{ow}, K_{oc}, and so forth, and toxicity values such as PNEC, EC50, bioaccumulation coefficients and bioconcentration factors.	Compilation of a well-rounded database of toxicity endpoint criteria. Generation of a list of key anthropogenic contaminants of concern.	Field collections and laboratory studies to identify key hydrologic-biogeochemical factors controlling uptake of geogenics.	Selection of metals of interest in relation to IWS basins. Field and laboratory characterization of organic matter. Initial microcosm (that is, exposure) studies.
Mid-term (2- to 5-yr)	Feeding experiments of organisms such as snails and fish, in complex mixtures of contaminants such as those in WWTP. In-situ mobile laboratory experiments using environmental complex mixtures.	Improvements to QSAR and DART modeling tools. Field studies and computational toxicity tools to investigate CECs and potential proxies that can be used to predict the risk of anthropogenic contaminants	Development and testing of a simple coupled hydrologic-biogeochemical model to predict geogenic bioavailability and uptake in focus systems.	Development of improved analytical techniques for organometallic complex detection. Bioaccumulation microcosm experiments.
Long-term (10-yr)	Results from database compilation, laboratory and field work systematically incorporated into improved biogeochemical process-based models throughout this 10-year period.	Linkages between ecotoxicology studies and improved models to GIS mapping tools.	Enhancement of particulate matter characterization (that is, e-DNA, hyperspectral imaging); development and testing of proxies for select metals and water quality constituents.	Detection of organometallic complexes, in-situ improvements to predictive models with respect to organometallic bioavailability and ecosystem effects

Expected Outcomes

Understanding the bio-exposure and uptake of AGC contributes to WMA priorities in water availability including quantity, quality, and support of beneficial uses and ecosystem health. Addressing questions surrounding these complex processes and mechanisms requires broad, interdisciplinary, cross-mission area approaches (fig. C2). The gaps in knowledge and approaches discussed here are not exhaustive but are considered some of the most pressing gaps to address to improve our predictive capabilities surrounding water quality. It is important to note that our recommendations can be coordinated with other objectives being developed by the WMA. Below are some key expected outcomes from this work:

- Identification of key metal species (as opposed to relying on total metal concentrations) and organic CECs contributing to bio-uptake and bioaccumulation concerns for aquatic organisms.
- Characterization of the speciation and bioavailability of metal and organic chemical associated particulate matter in IWS basins, improving predictive modeling.
- Determination of hydrologic-biogeochemical mechanisms contributing to residence time thresholds that play a key role in uptake of AGCs.
- Development of a framework to predict the bioavailability and uptake of organometallic complexes, based on metal and organic carbon sources unique to water bodies of concern, such as IWS basins.
- Improved analytical capabilities for rapid, cost-effective measurements of target organic chemical indicators indicative of various environmental stressors and anthropogenic sources.
- Improved analytical capabilities for measuring organometallic complexes. This type of measurement will be valuable to assess water quality and improve model inputs.
- Creation of a database of toxicity endpoint criteria for aquatic and human consumption for a prioritized list of chemicals, along with a method for normalizing these and providing a qualitative assessment tool associated with these toxicity values.
- Identification of key measurements that can be used as a proxy for anthropogenic contaminants to provide an alternative approach when discrete measurements of all contaminant types is cost prohibitive.
- Improvement of predictive modeling capabilities through the extensive development of QSAR and DART tools.
- Linkages between ecotoxicology models and GIS tools that can be used to assess water quality at variable (local to national) scales.

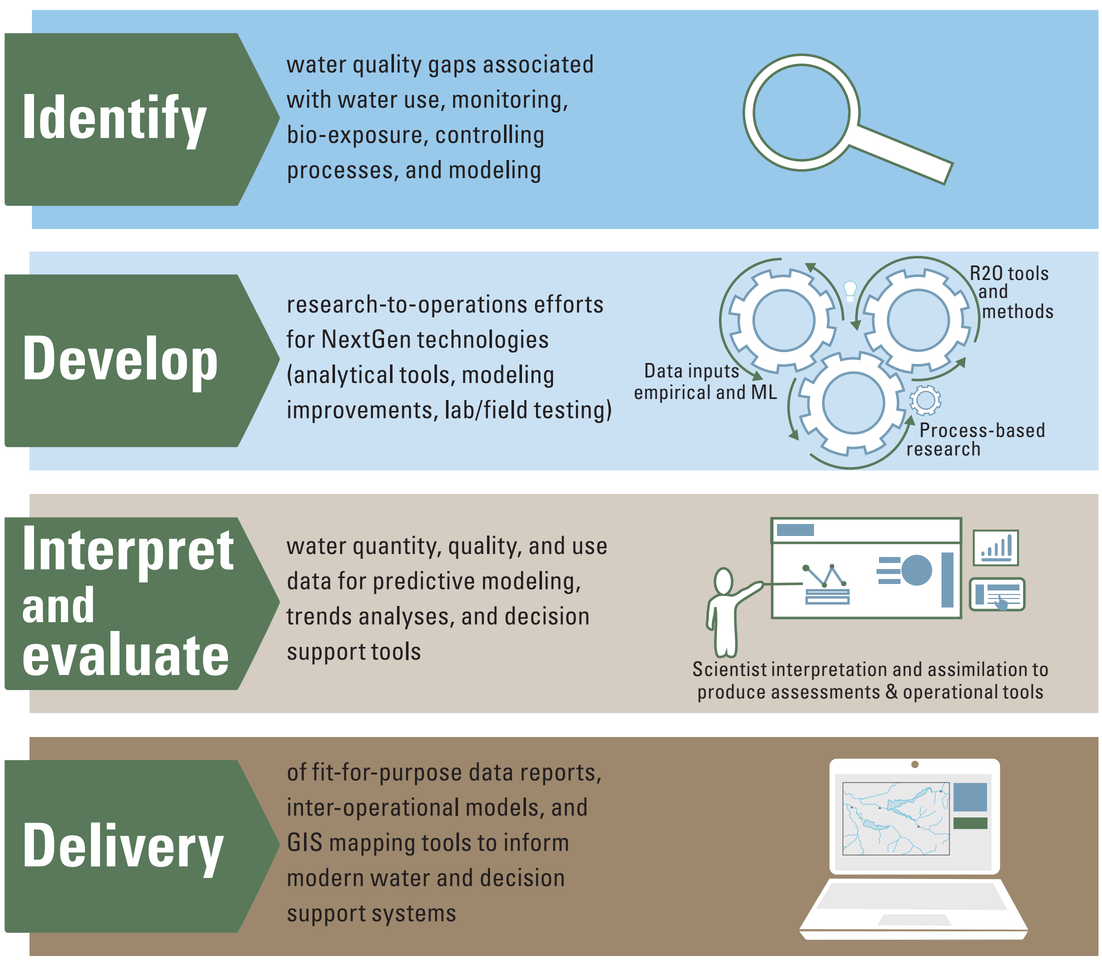


Figure C2. Diagram of a proposed U.S. Geological Survey (USGS) integrated interdisciplinary, cross-mission-area approach to deliver actionable water-availability science to address complex processes and mechanisms for solving knowledge gaps in anthropogenic and geogenic contaminant bioexposures affecting aquatic ecosystems. GIS, geographic information systems; ML, machine learning; and R2O, research to operation.

References Cited

Abbott, B.W., Bishop, K., Zarnetske, J.P., Minaudo, C., Chapin, F.S., III, Krause, S., Hannah, D.M., Conner, L., Ellison, D., Godsey, S.E., Plont, S., Marçais, J., Kolbe, T., Huebner, A., Frei, R.J., Hampton, T., Gu, S., Buhman, M., Sayedi, S.S., Ursache, O., Chapin, M., Henderson, K.D., and Pinay, G., 2019, Human domination of the global water cycle absent from depictions and perceptions: Nature Geoscience, v. 12, no. 7, p. 533–540, https://doi.org/10.1038/s41561-019-0374-y.

Agriculture & Environment Research Unit [AERU], 2021, PPDB—Pesticide properties database: Hertfordshire, U.K., University of Hertfordshire, Agriculture & Environment Research Unit [AERU], accessed November 1, 2021, at https://sitem.herts.ac.uk/aeru/ppdb/en/.

Ankley, G.T., Bennett, R.S., Erickson, R.J., Hoff, D.J., Hornung, M.W., Johnson, R.D., Mount, D.R., Nichols, J.W., Russom, C.L., Schmieder, P.K., Serrano, J.A., Tietge, J.E., and Villeneuve, D.L., 2010, Adverse outcome pathways—A conceptual framework to support ecotoxicology research and risk assessment: Environmental Toxicology and Chemistry, v. 29, no. 3, p. 730–741, https://doi.org/10.1002/etc.34.

Baines, S.B., and Fisher, N.S., 2001, Interspecific differences in the bioconcentration of selenite by phytoplankton and their ecological implications: Marine Ecology Progress Series, v. 213, p. 1–12, https://doi.org/10.3354/meps213001.

Barber, L.B., 2014, Emerging Contaminants, chap. 1.13 *of* Ahuja, S., ed., Comprehensive water quality and purification: Waltham, Mass., Elsevier, p. 245–266.

Barber, L.B., Keefe, S.H., Brown, G.K., Furlong, E.T., Gray, J.L., Kolpin, D.W., Meyer, M.T., Sandstrom, M.W., and Zaugg, S.D., 2013, Persistence and potential effects of complex organic contaminant mixtures in wastewater-impacted streams: Environmental Science & Technology, v. 47, no. 5, p. 2177–2188, https://doi.org/10.1021/es303720g.

Barber, L.B., Leenheer, J.A., Noyes, T.I., and Stiles, E.A., 2001, Nature and transformation of dissolved organic matter in treatment wetlands: Environmental Science & Technology, v. 35, no. 24, p. 4805–4816, https://doi.org/10.1021/es010518i.

Barber, L.B., Faunce, K.E., Bertolatus, D.W., Hladik, M.L., Jasmann, J.R., Keefe, S.H., Kolpin, D.W., Meyer, M.T., Rapp, J.L., Roth, D.A., and Vajda, A.M., 2022, Watershed-scale risk to aquatic organisms from complex chemical mixtures in the Shenandoah River: Environmental Science and Technology, v. 56, no. 2, p. 845–861, https://doi.org/10.1021/acs.est.1c04045.

Barber, L.B., Rapp, J.L., Kandel, C., Keefe, S.H., Rice, J., Westerhoff, P., Bertolatus, D.W., and Vajda, A.M., 2019, Integrated assessment of wastewater reuse, exposure risk, and fish endocrine disruption in the Shenandoah River watershed: Environmental Science & Technology, v. 53, no. 7, p. 3429–3440, https://doi.org/10.1021/acs.est.8b05655.

Barber, L.B., Vajda, A.M., Douville, C., Norris, D.O., and Writer, J.H., 2012, Fish endocrine disruption responses to a major wastewater treatment facility upgrade: Environmental Science & Technology, v. 46, no. 4, p. 2121–2131, https://doi.org/10.1021/es202880e.

Barnes, K.K., Kolpin, D.W., Furlong, E.T., Zaugg, S.D., Meyer, M.T., and Barber, L.B., 2008, A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States—I) Groundwater: Science of the Total Environment, v. 402, nos. 2–3, p. 192–200, https://doi.org/10.1016/j.scitotenv.2008.04.028.

Battaglin, W., Duncker, J., Terrio, P., Bradley, P., Barber, L., and DeCicco, L., 2020, Evaluating the potential role of bioactive chemicals on the distribution of invasive Asian carp upstream and downstream from river mile 278 in the Illinois waterway: Science of the Total Environment, v. 735, article 139458, p. XX, https://doi.org/10.1016/j.scitotenv.2020.139458.

Brack, W., Aissa, S.A., Backhaus, T., Dulio, V., Escher, B.I., Faust, M., Hilscherova, K., Hollender, J., Hollert, H., Müller, C., and Munthe, J., 2019, Effect-based methods are key—The European Collaborative Project SOLUTIONS recommends integrating effect-based methods for diagnosis and monitoring of water quality: Environmental Sciences Europe, v. 31, no. 1, 6 p., https://doi.org/10.1186/s12302-019-0192-2.

Bradley, P.M., Journey, C.A., Button, D.T., Carlisle, D.M., Clark, J.M., Mahler, B.J., Nakagaki, N., Qi, S.L., Waite, I.R., and Van Metre, P.C., 2016, Metformin and other pharmaceuticals widespread in wadeable streams of the southeastern United States: Environmental Science & Technology Letters, v. 3, no. 6, p. 243–249, https://doi.org/10.1021/acs.estlett.6b00170.

Bradley, P.M., Journey, C.A., Romanok, K.M., Barber, L.B., Buxton, H.T., Foreman, W.T., Furlong, E.T., Glassmeyer, S.T., Hladik, M.L., Iwanowicz, L.R., Jones, D.K., Kolpin, D.W., Kuivila, K.M., Loftin, K.A., Mills, M.A., Meyer, M.T., Orlando, J.L., Reilly, T.J., Smalling, K.L., and Villeneuve, D.L., 2017, Expanded target-chemical analysis reveals extensive mixed-organic-contaminant exposure in U.S. streams: Environmental Science & Technology, v. 51, no. 9, p. 4792–4802, https://doi.org/10.1021/acs.est.7b00012.

Bradley, P.M., Kolpin, D.W., Romanok, K.M., Smalling, K.L., Focazio, M.J., Brown, J.B., Cardon, M.C., Carpenter, K.D., Corsi, S.R., DeCicco, L.A., Dietze, J.E., Evans, N., Furlong, E.T., Givens, C.E., Gray, J.L., Griffin, D.W., Higgins, C.P., Hladik, M.L., Iwanowicz, L.R., Journey, C.A., Kuivila, K.M., Masoner, J.R., McDonough, C.A., Meyer, M.T., Orlando, J.L., Strynar, M.J., Weis, C.P., and Wilson, V.S., 2018, Reconnaissance of mixed organic and inorganic chemicals in private and public supply tapwaters at selected residential and workplace sites in the United States: Environmental Science & Technology, v. 52, no. 23, p. 13972–13985, https://doi.org/10.1021/acs.est.8b04622.

Brigham, M.E., Wentz, D.A., Aiken, G.R., and Krabbenhoft, D.P., 2009, Mercury cycling in stream ecosystems, 1—Water column chemistry and transport: Environmental Science & Technology, v. 43, no. 8, p. 2720–2725, https://doi.org/10.1021/es802694n.

Cain, D.J., Croteau, M.-N., Fuller, C.C., and Ringwood, A.H., 2016, Dietary uptake of Cu sorbed to hydrous iron oxide is linked to cellular toxicity and feeding inhibition in a benthic grazer: Environmental Science & Technology, v. 50, no. 3, p. 1552–1560, https://doi.org/10.1021/acs.est.5b04755.

Card, M.L., Gomez-Alvarez, V., Lee, W.-H., Lynch, D.G., Orentas, N.S., Lee, M.T., Wong, E.M., and Boethling, R.S., 2017, History of EPI Suite and future perspectives on chemical property estimation in US Toxic Substances Control Act new chemical risk assessments: Environmental Science, Processes & Impacts, v. 19, no. 3, p. 203–212, https://doi.org/10.1039/C7EM00064B.

Chapman, P.M., Adams, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P., eds., 2010, Ecological assessment of selenium in the aquatic environment: Boca Raton, CRC Press, 358 p.

Chen, H., Johnston, R.C., Mann, B.F., Chu, R.K., Tolic, N., Parks, J.M., and Gu, B., 2017, Identification of mercury and dissolved organic matter complexes using ultrahigh resolution mass spectrometry: Environmental Science & Technology Letters, v. 4, no. 2, p. 59–65, https://doi.org/10.1021/acs.estlett.6b00460.

Cory, R.M., and McKnight, D.M., 2005, Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter: Environmental Science & Technology, v. 39, no. 21, p. 8142–8149, https://doi.org/10.1021/es0506962.

Covert, S.A., Shoda, M.E., Stackpoole, S.M., and Stone, W.W., 2020, Pesticide mixtures show potential toxicity to aquatic life in U.S. streams, water years 2013–2017: Science of the Total Environment, v. 745, article 141285, 12 p., https://doi.org/10.1016/j.scitotenv.2020.141285.

Croteau, M.-N., Cain, D.J., and Fuller, C.C., 2017, Assessing the dietary bioavailability of metals associated with natural particles—Extending the use of the reverse labeling approach to zinc: Environmental Science & Technology, v. 51, no. 5, p. 2803–2810, https://doi.org/10.1021/acs.est.6b06253.

Croteau, M.-N., Fuller, C.C., Cain, D.J., Campbell, K.M., and Aiken, G., 2016, Biogeochemical controls of uranium bioavailability from the dissolved phase in natural freshwaters: Environmental Science & Technology, v. 50, no. 15, p. 8120–8127, https://doi.org/10.1021/acs.est.6b02406.

Croteau, M.-N., and Luoma, S.N., 2005a, Delineating copper accumulation pathways for the freshwater bivalve *Corbicula* using stable copper isotopes: Environmental Toxicology and Chemistry, v. 24, no. 11, p. 2871–2878, https://doi.org/10.1897/04-608R.1.

Croteau, M.-N., Luoma, S.N., and Stewart, A.R., 2005b, Trophic transfer of metals along freshwater food webs—Evidence of cadmium biomagnification in nature: Limnology and Oceanography, v. 50, no. 5, p. 1511–1519, https://doi.org/10.4319/lo.2005.50.5.1511.

de Paiva Magalhães, D., da Costa Marques, M.R., Baptista, D.F., and Buss, D.F., 2015, Metal bioavailability and toxicity in freshwaters: Environmental Chemistry Letters, v. 13, no. 1, p. 69–87, https://doi.org/10.1007/s10311-015-0491-9.

Eagles-Smith, C.A., Suchanek, T.H., Colwell, A.E., Anderson, N.L., and Moyle, P.B., 2008, Changes in fish diets and food web mercury bioaccumulation induced by an invasive planktivorous fish: Ecological Applications, v. 18, no. sp8, p. A213–A226, https://doi.org/10.1890/06-1415.1.

Faunce, K.E., Keefe, S.H., Barber, L.B., Jasmann, J.R., and Rapp, J.L., 2023, Modeling wastewater reuse and risk posed by wastewater-derived contaminants in the Potomac River Watershed: Journal of the American Water Resources Association, article JAWR-22-0077-P, 24 p., https://doi.org/10.1111/1752-1688.13110.

Fischer, A., Ter Laak, T., Bronders, J., Desmet, N., Christoffels, E., van Wezel, A., and van der Hoek, J.P., 2017, Decision support for water quality management of contaminants of emerging concern: Journal of Environmental Management, v. 193, p. 360–372, https://doi.org/10.1016/j.jenvman.2017.02.002.

Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Barber, L.B., and Thurman, M.E., 2008, A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States—II) Untreated drinking water sources: Science of the Total Environment, v. 402, nos. 2–3, p. 201–216, https://doi.org/10.1016/j.scitotenv.2008.02.021.

Gadd, G.M., and Griffiths, A.J., 1977, Microorganisms and heavy metal toxicity: Microbial Ecology, v. 4, no. 4, p. 303–317, https://doi.org/10.1007/BF02013274.

Gramatica, P., Cassani, S., and Sangion, A., 2016, Aquatic ecotoxicity of personal care products—QSAR models and ranking for prioritization and safer alternatives' design: Green Chemistry, v. 18, no. 16, p. 4393–4406, https://doi.org/10.1039/C5GC02818C.

Griscom, S.B., Fisher, N.S., and Luoma, S.N., 2000, Geochemical influences on assimilation of sediment-bound metals in clams and mussels: Environmental Science & Technology, v. 34, no. 1, p. 91–99, https://doi.org/10.1021/es981309+.

Hansen, A.M., Kraus, T.E.C., Pellerin, B.A., Fleck, J.A., Downing, B.D., and Bergamaschi, B.A., 2016, Optical properties of dissolved organic matter (DOM)—Effects of biological and photolytic degradation: Limnology and Oceanography, v. 61, no. 3, p. 1015–1032, https://doi.org/10.1002/lno.10270.

Helms, J.R., Stubbins, A., Ritchie, J.D., Minor, E.C., Kieber, D.J., and Mopper, K., 2008, Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter: Limnology and Oceanography, v. 53, no. 3, p. 955–969, https://doi.org/10.4319/lo.2008.53.3.0955.

Hoffmann, M., Mikutta, C., and Kretzschmar, R., 2013, Arsenite binding to natural organic matter—Spectroscopic evidence for ligand exchange and ternary complex formation: Environmental Science & Technology, v. 47, no. 21, p. 12165–12173, https://doi.org/10.1021/es4023317.

Johnson, R.C., Stewart, A.R., Limburg, K.E., Huang, R., Cocherell, D., and Feyrer, F., 2020, Lifetime chronicles of selenium exposure linked to deformities in an imperiled migratory fish: Environmental Science & Technology, v. 54, no. 5, p. 2892–2901, https://doi.org/10.1021/es4023317.

Kandel, C.M., Rapp, J.L., and Barber, L.B., 2017, Shenandoah River Accumulated Wastewater Ratio Mapper: U.S. Geological Survey data release. [Superseded by ver.2.0, February 2019, which is available at https://doi.org/10.5066/F7RF5S8X.]

Kim, S., Chen, J., Cheng, T., Gindulyte, A., He, J., He, S., Li, Q., Shoemaker, B.A., Thiessen, P.A., Yu, B., Zaslavsky, L., Zhang, J., and Bolton, E.E., 2020, PubChem in 2021—New data content and improved web interfaces: Nucleic Acids Research, v. 49, no. D1, p. D1388–D1395, https://doi.org/10.1093/nar/gkaa971.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., and Buxton, H.T., 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000—A national reconnaissance: Environmental Science & Technology, v. 36, no. 6, p. 1202–1211, https://doi.org/10.1021/es011055j.

Lamelas, C., Wilkinson, K.J., and Slaveykova, V.I., 2005, Influence of the composition of natural organic matter on Pb bioavailability to microalgae: Environmental Science & Technology, v. 39, no. 16, p. 6109–6116, https://doi.org/10.1021/es050445t.

Lavoie, R.A., Jardine, T.D., Chumchal, M.M., Kidd, K.A., and Campbell, L.M., 2013, Biomagnification of mercury in aquatic food webs—A worldwide meta-analysis: Environmental Science & Technology, v. 47, no. 23, p. 13385–13394, https://doi.org/10.1021/es403103t.

Lepak, R.F., Krabbenhoft, D.P., Ogorek, J.M., Tate, M.T., Bootsma, H.A., and Hurley, J.P., 2015, Influence of *Cladophora*–quagga mussel assemblages on nearshore methylmercury production in Lake Michigan: Environmental Science & Technology, v. 49, no. 13, p. 7606–7613, https://doi.org/10.1021/es506253v.

Lepak, J.M., Robinson, J.M., Kraft, C.E., and Josephson, D.C., 2009, Changes in mercury bioaccumulation in an apex predator in response to removal of an introduced competitor: Ecotoxicology, v. 18, no. 5, p. 488–498, https://doi.org/10.1007/s10646-009-0306-5.

Lescord, G.L., Emilson, E.J.S., Johnston, T.A., Branfireun, B.A., and Gunn, J.M., 2018, Optical properties of dissolved organic matter and their relation to mercury concentrations in water and biota across a remote freshwater drainage basin: Environmental Science & Technology, v. 52, no. 6, p. 3344–3353, https://doi.org/10.1021/acs.est.7b05348.

Luoma, S.N., and Rainbow, P.S., 2009, Metal contamination in aquatic environments—Science and lateral management: Integrated Environmental Assessment and Management, v. 5, no. 3, p. 492, https://doi.org/10.1897/1551-3793-5.3.492.

Masoner, J.R., Kolpin, D.W., Cozzarelli, I.M., Barber, L.B., Burden, D.S., Foreman, W.T., Forshay, K.J., Furlong, E.T., Groves, J.F., Hladik, M.L., Hopton, M.E., Jaeschke, J.B., Keefe, S.H., Krabbenhoft, D.P., Lowrance, R., Romanok, K.M., Rus, D.L., Selbig, W.R., Williams, B.H., and Bradley, P.M., 2019, Urban stormwater—An overlooked pathway of extensive mixed contaminants to surface and groundwaters in the United States: Environmental Science & Technology, v. 53, no. 17, p. 10070–10081, https://doi.org/10.1021/acs.est.9b02867.

Mebane, C.A., Chowdhury, M.J., De Schamphelaere, K.A.C., Lofts, S., Paquin, P.R., Santore, R.C., and Wood, C.M., 2020, Metal bioavailability models—Current status, lessons learned, considerations for regulatory use, and the path forward: Environmental Toxicology and Chemistry, v. 39, no. 1, p. 60–84, https://doi.org/10.1002/etc.4560.

Medlock Kakaley, E.K., Blackwell, B.R., Cardon, M.C., Conley, J.M., Evans, N., Feifarek, D.J., Furlong, E.T., Glassmeyer, S.T., Gray, L.E., Hartig, P.C., Kolpin, D.W., Mills, M.A., Rosenblum, L., Villeneuve, D.L., and Wilson, V.S., 2020, De facto water reuse—Bioassay suite approach delivers depth and breadth in endocrine active compound detection: Science of the Total Environment, v. 699, article 134297, 12 p., https://doi.org/10.1016/j.scitotenv.2019.134297.

Norman, J.E., Toccalino, P.L., and Morman, S.A., 2018, Health-based screening levels for evaluating water-quality data (2d ed.): U.S. Geological Survey web page, https://doi.org/10.5066/F71C1TWP.

Nowell, L.H., Norman, J.E., Moran, P.W., Martin, J.D., and Stone, W.W., 2014, Pesticide toxicity index—A tool for assessing potential toxicity of pesticide mixtures to freshwater aquatic organisms: Science of the Total Environment, v. 476–477, p. 144–157, https://doi.org/10.1016/j.scitotenv.2013.12.088.

Omar, T.F.T., Ahmad, A., Aris, A.Z., and Yusoff, F.M., 2016, Endocrine disrupting compounds (EDCs) in environmental matrices—Review of analytical strategies for pharmaceuticals, estrogenic hormones, and alkylphenol compounds: TrAC Trends in Analytical Chemistry, v. 85, p. 241–259, https://doi.org/10.1016/j.trac.2016.08.004.

Ortiz de García, S.A., Pinto, G.P., García-Encina, P.A., and Irusta-Mata, R., 2013, Ranking of concern, based on environmental indexes, for pharmaceutical and personal care products—An application to the Spanish case: Journal of Environmental Management, v. 129, p. 384–397, https://doi.org/10.1016/j.jenvman.2013.06.035.

Ortiz de García, S.A., Pinto, G.P., García-Encina, P.A., and Irusta-Mata, R., 2014, Ecotoxicity and environmental risk assessment of pharmaceuticals and personal care products in aquatic environments and wastewater treatment plants: Ecotoxicology, v. 23, no. 8, p. 1517–1533, https://doi.org/10.1007/s10646-014-1293-8.

Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods book 6, chap. A43, 497 p., https://doi.org/10.3133/tm6A43.

Pavan, M., and Worth, A., 2008a, A set of case studies to illustrate the applicability of DART (decision analysis by ranking techniques) in the ranking of chemicals: Joint Research Center Scientific and Technical Reports, no. EUR 23481 EN–2008, 82 p., accessed November 1, 2021 at https://publications.jrc.ec.europa.eu/repository/bitstream/JRC47007/applicability%20of%20dart_eur%20report_final.pdf.

Pavan, M., and Worth, A.P., 2008b, Publicly-accessible QSAR software tools developed by the Joint Research Centre: SAR and QSAR in Environmental Research, v. 19, nos. 7–8, p. 785–799, https://doi.org/10.1080/10629360802550390.

Ponton, D.E., Graves, S.D., Fortin, C., Janz, D., Amyot, M., and Schiavon, M., 2020, Selenium interactions with algae—Chemical processes at biological uptake sites, bioaccumulation, and intracellular metabolism: Plants, v. 9, no. 4, special issue, article 528, 26 p., https://doi.org/10.3390/plants9040528.

Presser, T.S., and Luoma, S.N., 2010, A methodology for ecosystem-scale modeling of selenium: Integrated Environmental Assessment and Management, v. 6, no. 4, p. 685–710, https://doi.org/10.1002/ieam.101.

Rainbow, P.S., and Luoma, S.N., 2011, Metal toxicity, uptake and bioaccumulation in aquatic invertebrates—Modelling zinc in crustaceans: Aquatic Toxicology, v. 105, nos. 3–4, p. 455–465, https://doi.org/10.1016/j.aquatox.2011.08.001.

Reemtsma, T., and These, A., 2005, Comparative investigation of low-molecular-weight fulvic acids of different origin by SEC-Q-TOF-MS—New insights into structure and formation: Environmental Science & Technology, v. 39, no. 10, p. 3507–3512, https://doi.org/10.1021/es0480466.

Reinfelder, J.R., Fisher, N.S., Luoma, S.N., Nichols, J.W., and Wang, W.-X., 1998, Trace element trophic transfer in aquatic organisms—A critique of the kinetic model approach: Science of the Total Environment, v. 219, nos. 2–3, p. 117–135, https://doi.org/10.1016/S0048-9697(98)00225-3.

Ren, J., Fan, W., Wang, X., Ma, Q., Li, X., Xu, Z., and Wei, C., 2017, Influences of size-fractionated humic acids on arsenite and arsenate complexation and toxicity to *Daphnia magna*: Water Research, v. 108, p. 68–77, https://doi.org/10.1016/j.watres.2016.10.052.

Roditi, H.A., Fisher, N.S., and Sañudo-Wilhelmy, S.A., 2000, Uptake of dissolved organic carbon and trace elements by zebra mussels: Nature, v. 407, article 6800, p. 78–80, https://doi.org/10.1038/35024069.

Sánchez-Marín, P., Lorenzo, J.I., Blust, R., and Beiras, R., 2007, Humic acids increase dissolved lead bioavailability for marine invertebrates: Environmental Science & Technology, v. 41, no. 16, p. 5679–5684, https://doi.org/10.1021/es070088h.

Sangion, A., and Gramatica, P., 2016, PBT assessment and prioritization of contaminants of emerging concern: Pharmaceuticals: Environmental Research, v. 147, p. 297–306, https://doi.org/10.1016/j.envres.2016.02.021.

Schlekat, C.E., Lee, B.-G., and Luoma, S.N., 2002, Assimilation of selenium from phytoplankton by three benthic invertebrates—Effect of phytoplankton species: Marine Ecology Progress Series, v. 237, p. 79–85, https://doi.org/10.3354/meps237079.

Selin, N.E., 2009, Global Biogeochemical Cycling of Mercury—A review: Annual Review of Environment and Resources, v. 34, no. 1, p. 43–63, https://doi,org/10.1146/annurev.environ.051308.084314.

Shi, W., Fang, X., Wu, X., Zhang, G., Que, W., and Li, F., 2018, Alteration of bioaccumulation mechanisms of Cu by microalgae in the presence of natural fulvic acids: Chemosphere, v. 211, p. 717–725, https://doi.org/10.1016/j.chemosphere.2018.07.200.

Shindo, H., and Brown, T.L., 1965, Infrared spectra of complexes of L-cysteine and related compounds with zinc(II), cadmium(II), mercury(II), and lead(II): Journal of the American Chemical Society, v. 87, no. 9, p. 1904–1909, https://doi.org/10.1021/ja01087a013.

Spehar, R.L., Fiandt, J.T., Anderson, R.L., and DeFoe, D.L., 1980, Comparative toxicity of arsenic compounds and their accumulation in invertebrates and fish: Archives of Environmental Contamination and Toxicology, v. 9, no. 1, p. 53–63, https://doi.org/10.1007/BF01055499.

Stewart, A.R., Grosell, M., Buchwalter, D.B., Fisher, N.S., Luoma, S.N., Matthews, T., Orr, P., and Wang, W.-X., 2010, Bioaccumulation and trophic transfer of selenium, chap 5 *of* Chapman, P.M., Adams, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., and Shaw, P.D., eds., Ecological assessment of selenium in the aquatic environment: Boca Raton, Flor., CRC Press, p. 93–140.

Stewart, A.R., Luoma, S.N., Schlekat, C.E., Doblin, M.A., and Hieb, K.A., 2004, Food web pathway determines how selenium affects aquatic ecosystems—A San Francisco Bay case study: Environmental Science & Technology, v. 38, no. 17, p. 4519–4526, https://doi.org/10.1021/es0499647.

Stewart, A.R., and Malley, D.F., 1999, Effect of metal mixture (Cu, Zn, Pb, and Ni) on cadmium partitioning in littoral sediments and its accumulation by the freshwater macrophyte *Eriocaùlon septangulàre*: Environmental Toxicology and Chemistry, v. 18, no. 3, p. 436–447, https://doi.org/10.1002/etc.5620180311.

Stewart, A.R., Saiki, M.K., Kuwabara, J.S., Alpers, C.N., Marvin-DiPasquale, M., and Krabbenhoft, D.P., 2008, Influence of plankton mercury dynamics and trophic pathways on mercury concentrations of top predator fish of a mining-impacted reservoir: Canadian Journal of Fisheries and Aquatic Sciences, v. 65, no. 11, p. 2351–2366, https://doi.org/10.1139/F08-140.

Tan, K.H., and Giddens, J.E., 1972, Molecular weights and spectral characteristics of humic and fulvic acids: Geoderma, v. 8, no. 4, p. 221–229, https://doi.org/10.1016/0016-7061(72)90013-4.

Tesoriero, A.J., Erickson, M.L., Conaway, C.H., Tomaszewski, E.J., and Green, C.T., 2024, Knowledge gaps and opportunities for understanding water-quality processes affecting water availability for beneficial uses: U.S. Geological Survey Open-File Report 2023–1086, 81 p., https://doi.org/10.3133/ofr20231086.

Thurman, E.M., 1985, Organic geochemistry of natural waters, part *of* Developments in Biogeochemistry, v. 2: Springer Dordrecht, 497 p., available at https://doi.org/10.1007/978-94-009-5095-5.

U.S. Environmental Protection Agency [EPA], 1999, Protocol for developing sediment TMDLs (1st ed.): U.S Environmental Protection Agency, Office of Water, no. EPA-841-B-99-004, 143 p. [Available from https://www.epa.gov/nscep.]

U.S. Environmental Protection Agency [EPA], 2012, Estimation program interface (EPI) Suite for Microsoft Windows (4.11 ed.): U.S. Environmental Protection Agency software release, accessed November 1, 2023, at https://www.epa.gov/tsca-screening-tools/download-epi-suitetm-estimation-program-interface-v411.

U.S. Environmental Protection Agency [EPA], 2016, Computational toxology chemicals dashboard (CompTox dashboard): U.S. Environmental Protection Agency database, accessed November 1, 2021, at https://comptox.epa.gov/.

U.S. Environmental Protection Agency [EPA], 2017, National Summary of State Information: U.S. Environmental Protection Agency, accessed January 2021, at https://iaspub.epa.gov/waters10/attains_nation_cy.control. [Also available at https://www.epa.gov/waterdata/attains]

U.S. Environmental Protection Agency [EPA], 2021a, Aquatic life benchmarks and ecological risk assessments for registered pesticides: U.S. Environmental Protection Agency database, accessed November 1, 2021, at https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk.

U.S. Environmental Protection Agency [EPA], 2021b, National recommended water quality criteria—Aquatic life criteria table: U.S. Environmental Protection Agency database, accessed November 1, 2021, at https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table.

Vajda, A.M., Barber, L.B., Gray, J.L., Lopez, E.M., Bolden, A.M., Schoenfuss, H.L., and Norris, D.O., 2011, Demasculinization of male fish by wastewater treatment plant effluent: Aquatic Toxicology, v. 103, nos. 3–4, p. 213–221, https://doi.org/10.1016/j.aquatox.2011.02.007.

Van Metre, P.C., Waite, I.R., Qi, S., Mahler, B., Terando, A., Wieczorek, M., Meador, M., Bradley, P., Journey, C., Schmidt, T., and Carlisle, D., 2019, Projected urban growth in the southeastern USA puts small streams at risk: PLOS ONE, v. 14, no. 10, article e0222714, 17 p., https://doi.org/10.1371/journal.pone.0222714.

Velma, V., Vutukuru, S.S., and Tchounwou, P.B., 2009, Ecotoxicology of hexavalent chromium in freshwater fish—A critical review: Reviews on Environmental Health, v. 24, no. 2, p. 129–146, https://doi.org/10.1515/REVEH.2009.24.2.129.

Voets, J., Bervoets, L., and Blust, R., 2004, Cadmium bioavailability and accumulation in the presence of humic acid to the zebra mussel, *Dreissena polymorpha*: Environmental Science & Technology, v. 38, no. 4, p. 1003–1008, https://doi.org/10.1021/es034742e.

Wang, W.X., Fisher, N.S., and Luoma, S.N., 1996, Kinetic determinations of trace element bioaccumulation in the mussel *Mytilus edulis*: Marine Ecology Progress Series, v. 140, p. 91–113, https://doi.org/10.3354/meps140091.

Wang, Y., Hu, Y., Yang, C., Wang, Q., and Jiang, D., 2019, Variations of DOM quantity and compositions along WWTPs-river-lake continuum—Implications for watershed environmental management: Chemosphere, v. 218, p. 468–476, https://doi.org/10.1016/j.chemosphere.2018.11.037.

Weisman, R. J., Barber, L. B., Rapp, J. L., and Ferreira, C. M., 2019, De facto reuse and disinfection by-products in drinking water systems in the Shenandoah River watershed: Environmental Science: Water Research & Technology, v. 5, no. 10, p. 1699–1708, https://doi.org/10.1039/C9EW00326F.

Zhang, L., Zhang, Y., Zhu, M., Chen, L., and Wu, B., 2023, A critical review on quantitative evaluation of aqueous toxicity in water quality assessment: Chemosphere, article no. 140159, 12 p., https://doi.org/10.1016/j.chemosphere.2023.140159.

Zhao, C.-M., Campbell, P.G.C., and Wilkinson, K.J., 2016, When are metal complexes bioavailable?: Environmental Chemistry, v. 13, no. 3, p. 425–433, https://doi.org/10.1071/EN15205.

Knowledge Gaps and Opportunities in Water-Quality Drivers of Aquatic Ecosystem Health
Edited by Judson W. Harvey, Christopher H. Conaway, Mark M. Dornblaser, Allen C. Gellis, A. Robin Stewart, and Christopher T. Green
[Also see https://doi.org/10.3133/ofr20231085]

Chapter D

Fine Sediment Drivers of Aquatic Ecosystem Health

By Allen C. Gellis, Judson W. Harvey, Christopher H. Conaway, and Nancy T. Baker

Purpose and Scope

This chapter addresses knowledge gaps that, if filled, could improve predictions of aquatic ecosystem health as affected by fine sediment drivers. The gaps identified in this chapter are not intended to be comprehensive but are instead focused on key opportunities to fill knowledge gaps for the U.S. Geological Survey (USGS) Water Resources Mission Area (WMA, https://www.usgs.gov/mission-areas/water-resources).

Statement of the Problem

The erosion, transport and delivery of fine-grained sediment is a major issue in the United States (U.S. Environmental Protection Agency [EPA], 1999). Key Findings of the National Water Quality Inventory Report to Congress (EPA, 2017c), which examined 3.5 million miles of our Nation's rivers and streams, indicated sediment, along with pathogens and nutrients was the leading cause of pollution. Excessive sediment has caused loss of channel conveyance and reduction of reservoir storage capacity, as well as facilitated transport and storage of sorbed contaminants such as nutrients, metals, and anthropogenic contaminants (Owens and others, 2005; Larsen and others, 2010; Collins and others, 2017; DeGood, 2020). Furthermore, excess fine sediment degrades river ecosystems by clouding water supply and burying streambeds, reducing light availability for productivity, consuming oxygen, and decreasing overall habitat quality and food supply (Sutherland and others, 2010; Kondolf and others, 2014).

Fine-grained sediment (or "fine sediment") is typically the largest proportion of the suspended load in channels, typically less than 0.063 millimeters (mm) in diameter, and with a large surface area for chemical sorption of a wide range of constituents (Turowski and others, 2010). Fine sediment consists of silts, clays, and organic matter including living algal cells and bacteria. If measured as suspended sediment concentration during stormflow, it may include larger-grained sediments such as sand or flocculated fine particles with an effective diameter greater than 0.063 mm (Owens and others, 2005).

As a pollutant, the importance of sediment to stakeholders is indicated by the EPA's National Rivers and Streams Assessment that found that excess streambed sedimentation occurred in 15 percent of river and stream lengths (EPA, 2020). Impairments by fine sediment were among the most frequently reported impairments in United States rivers and streams, with fine sediment ranking 6th overall in total nationwide reporting of impairments (EPA, 2017c). Fine sediment impairments also are widespread, ranking 2nd in rating as a "top 5 impairment" in 16 out of 21 (76 percent) of the water resource accounting regions used by the EPA to summarize water quality impairments (listed under section 303(d) of the Clean Water Act [CWA; 33 U.S.C 1251, section 303(d), https://www.epa.gov/tmdl]) using information similar to what can be found in the National Summary of Impaired Waters and total maximum daily load (TMDL) information (EPA, 2017b).

Understanding and quantifying the transport of fine sediment is central to the U.S. Geological Survey (USGS) Water Mission Area's (WMA's) goal of identifying causes of impaired water quality in aquatic ecosystems. Background concentrations of fine suspended sediment in healthy aquatic ecosystems vary greatly with geologic setting and land use (Robertson and others, 2006), and therefore no comprehensive national standard exists for fine sediment in streams. The focus is on measuring and modeling the effects of fine sediment on aquatic productivity and organism health, as well as drinking water quality and loss of reservoir storage. In order to manage the excess fine sediment problem and its degradation of the Nation's rivers, it is imperative to understand the sources of fine sediment to rivers and its transit and storage times in the river network, as well as its role in transporting other constituents of concern (for example, phosphorus, metals), and the resulting effects on aquatic organisms and ecosystem functions (Gellis and Walling, 2011; Mukundan and others, 2012; Collins and others, 2017). The sources, transport, and fate of sediment and associated contaminants need to be identified to determine potential effectiveness of management strategies that will protect ecosystem services and water supply.

This chapter presents the principal knowledge gaps that the USGS identified in fine sediment drivers of aquatic ecological health. These gaps are hindering WMA's capabilities to deliver scientific information to stakeholders who are responsible for managing a growing problem with excess fine sediment in the Nation's waterways. The four knowledge gaps we identified are:

11. Understanding fine sediment sources and connectivity through the Nation's waterways,

12. How fine sediment sources are apportioned between erosion in channel corridors versus uplands,

13. Predicting fine sediment-associated contaminants and biophysical drivers of eco-health, and

14. Ability to forecast climate and land-use driven alterations of fine sediment.

Here, we support the selection of these major knowledge gaps for fine sediment with a brief review of existing knowledge and capabilities, priorities for improvement, and initial suggestions for approaches and timelines. We discuss how renewed effort in these areas can support stakeholders who need to predict where, when, and how much fine sediment will impair aquatic ecosystems, water supply impoundments, and navigation channels.

Status of Knowledge and Capabilities Including Key Gaps and Limitations

Figure D1 illustrates the sources and storage areas of fine sediment in uplands and within the channel corridor that affect aquatic ecosystems. The general status of knowledge and information about fine sediment and related water-quality drivers is summarized in table D1, and includes fine sediment gaps, rationale, metrics and modeling, and key references. Throughout this chapter we summarize information about driving physical and biological processes and human influences, as well as the numbers and types of nationwide EPA 303(d) listings of impairments of surface waters. A supplementary table (table D2) provides information about primary constituents of concern and closely associated indicator measurements and physiochemical parameters. Table D2 provides notations and links to additional information about benchmarks for aquatic life, trends in exceedances of those benchmarks, along with notations about the general level of USGS data that are available for analysis.

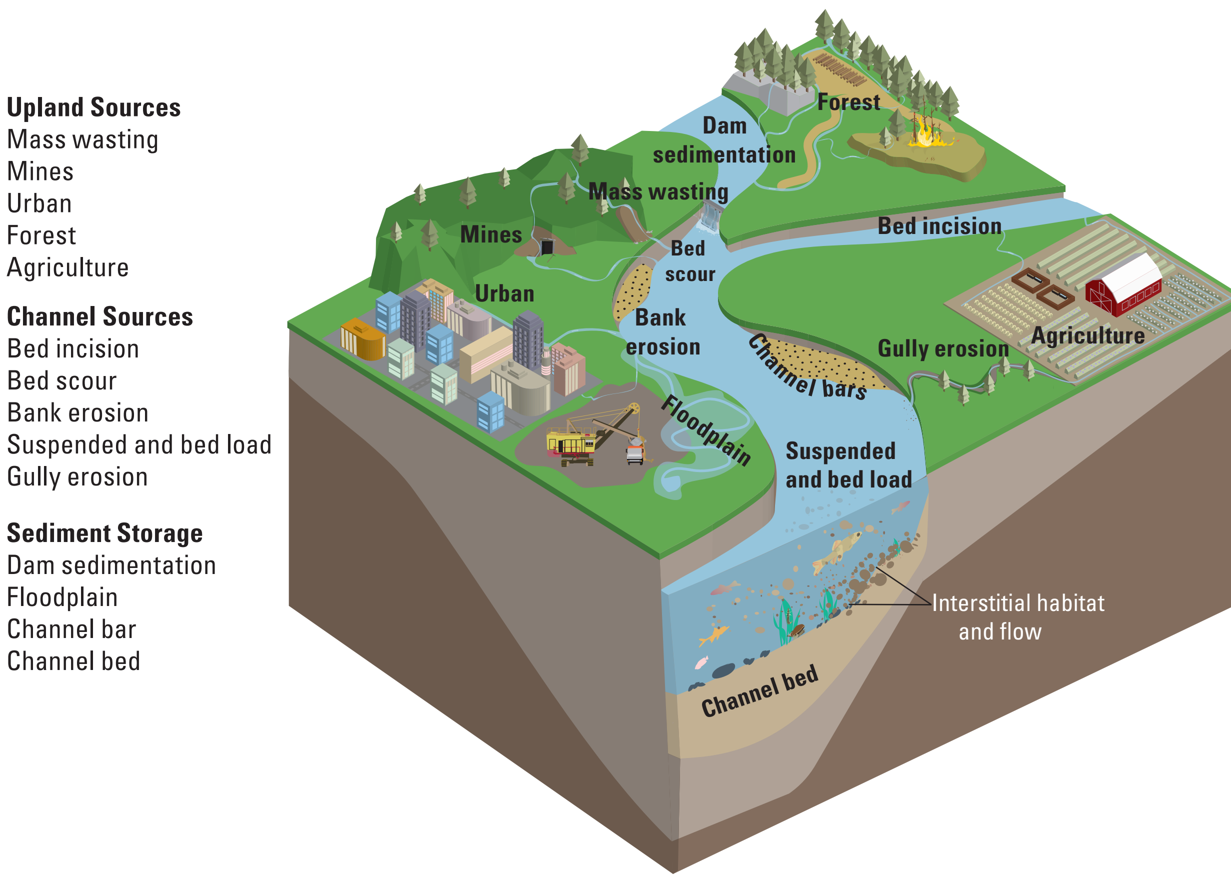


Figure D1. Diagram of drivers, sources, and storages of fine sediment and particle-associated contaminants affecting aquatic ecosystems and the four principal knowledge gaps identified by the U.S. Geological Survey (USGS) for fine sediment drivers of aquatic ecological health.

Table D1. Summary of fine sediment knowledge gaps, including background rationale, metrics, modeling, and key references for water-quality drivers of aquatic ecosystem health identified by the U.S. Geological Survey (USGS).

[SPARROW, SPAtially Referenced Regression On Watershed attribute (https://www.usgs.gov/software/sparrow-modeling-program); GIS, geographic information systems.]

What	Gap	Why	How—Measurements and modeling approaches	References
Sediment sourcing	We do not have a comprehensive national understanding of fine sediment sources, that is, is sediment coming from upland erosion (agricultural areas, construction sites, or urban areas) vs. riparian areas or in-stream sources (stream bank erosion) vs. wetland or reservoir exceeding its storage capacity?	To mitigate fine sediment as a pollutant, it is imperative to identify sources. We do not have a comprehensive national strategy to identify and manage sources of excess fine sediment.	Sediment fingerprinting, sediment budgets, expanded suspended sediment concentration monitoring, use of turbidity as a surrogate	Gellis and Walling, 2011; Larsen and others, 2015; Gellis and others, 2016; Gellis and Gorman Sanisaca, 2018; Collins and others, 2020.
Bank erosion	We do not have models that can reliably estimate bank erosion contributions and separate them from upland sources. Coupled with nutrient and contaminant data of streambanks, enhanced models could provide insight into the role streambank erosion plays in nutrient and contaminant budgets.	Streambanks have been shown to be an important (often the dominant) sediment source and in many watersheds a contributor of sediment-associated contaminants. It is therefore important to acquire new data and build modeling capacity to estimate this process.	Physical models and statistical models both have their advantages and shortcomings. The USGS SPARROW model provides an excellent platform to incorporate metric based physical model results into a statistical model. However, the problem of scaling between regional model predictions and local watershed outcomes that are of concern to stakeholders remains a key gap in sediment prediction.	Sekely and others, 2002; Van Metre and Mahler, 2005; Ishee and others, 2015; Schmadel and others, 2019; Noe and others, 2020a.
Sediment contamination	We need to understand the factors controlling new and emerging sediment-related contaminants, in stream (with special focus on emerging contaminants) and partition their sources between upland (urban and agriculture) and channel corridor.	Assessments of trends in recent and emerging chemicals of concern indicate various upland sources and their prevalence in river networks. We need better understanding of the sources, sinks, and transport pathways of these chemicals to effectively mitigate contamination through forensic tools.	Physical and statistical models to assess contaminant distribution and sourcing from depositional storage areas, such as ponds and reservoirs, examine links to water quality trends, examine sources and drivers of sediment-water partitioning, for example, redox, pH, salinity.	Wainwright and others, 2011; Schmadel and others, 2019; Gellis and others, 2020.
Sediment connectivity	We need to understand how sediment sources are connected to the fluvial systems.	To understand the transit and residence time of sediment, landscape elements controlling connectivity need to be understood.	Lidar, GIS analysis, terrain analysis, modeling tools for understanding the links and feedback of erosion, transport and delivery also include watershed hydrologic assessments, such as water balance, time-varying flow paths, storage-streamflow relations, ecohydrology, and so forth.	Borselli and others, 2008; Karwan and others, 2018) Bracken and others, 2015; Crema and Cavalli, 2018; Gellis and others, 2019.
Sediment age dating	We have little to no understanding of the age of channel deposited sediment and suspended sediment.	Unspecified sediment storage processes may vastly delay the effectiveness of management practices on downstream water quality and ecology	Precipitation fallout radionuclides, other age tracers (for example sediment associated contaminants where the location and time of "spill" into the river is known).	Skalak and Pizzuto, 2010; Gellis and others, 2017; Bernhardt and others, 2018.

Table D1.—Continued

What	Gap	Why	How—Measurements and modeling approaches	References
Turbidity[1]	Water-column light attenuation by suspended sediment decreases water clarity and photic depth, but its spatial and temporal variation and trends in the United States are poorly known; Its control on productivity, and on biological oxygen demand have not been widely estimated	Light attenuation by turbidity; turbidity is important because it affects primary productivity and food quality for healthy food webs, as well as contributing to excessive oxygen consumption that may often lead to hypoxia.	Harmonization of real-time and discrete turbidity data and analysis and remote sensing information, combined with related prediction of light attenuation, providing support for improved controls on primary productivity and ecosystem respiration in rivers.	Bussi and others, 2021; Savoy and Harvey, 2021.
Climate change drivers	We have little knowledge about how climate change affects sediment supply and transport.	In order for the management community to prepare for future sediment changes resulting from climate change, it is important to understand how climate change may affect the delivery of fine sediment to streams.	Suspended sediment, bedload, sediment budgets, sediment fingerprinting, and sediment and nutrient modeling.	Asselman, 1995; Collins and others, 2020; Moragoda and Cohen, 2020.

[1]Turbidity can be used as a proxy for suspended sediment concentration and optical clarity from which light attenuation, photic depth, primary productivity, and other outcomes for ecosystem can be estimated.

Two field measurements are commonly used to quantify fine sediment in streams: total suspended-solids (TSS) and suspended-sediment concentrations (SSC). At present there are no quantitative national benchmarks for TSS and SSC to protect aquatic life. The closest to a national criterion that exists is a narrative standard in the EPA's "Gold Book" (EPA, 1986) that is supported by discussion in Berry and others (2003). The standard reads:

> "Settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more than 10 percent from the seasonally established norm for aquatic life." (EPA, 1986, p. 268).

Thus, the effects of fine sediment on light attenuation and resulting reduction in productivity and food webs are recognized, but not regulated at the National level. Each State often develops their own criteria (Berry and others, 2003) which may be better suited to account for how sediment concentrations and loads vary across the United States in response to climate, geology, and land use (Simon and others, 2004).

Aquatic ecosystems have an amount of fine sediment that varies according to contributing area, parent geology, grain size of sediment in channel bed, land use and sediment sources, and degree of organic carbon (OC) loading from the terrestrial system. The degree of fine sediment retention in the channel network is affected by flow, slope and roughness characteristics of the channel and floodplain, as well as by the rate of breakdown of fine particulate organic matter by decomposition. The "right" amount of fine sediment for an ecosystem varies but is usually present in a moderate amount at the appropriate time of year with characteristics of grain size and organic content that do not negatively affect aquatic habitats or food webs (Vannote and others, 1980; Resh and others, 1988; Wohl and others, 2007; Wohl and others, 2017). For example, coarse and fine particulate organic matter (CPOM and FPOM) input are crucial to detrital based aquatic food webs however too much FPOM during warm summer months may raise biological oxygen (O) demand and cause harm by creating hypoxic or anoxic conditions in the sediment and (or) the water column (Bernhardt and others, 2018).

One of the negative effects of fine sediment includes excessive amounts affecting biohabitats (Jones and others, 2012; Collins and others, 2015; Collins and others, 2017). Fine sediment has fundamental effects on hydraulics, river form, growth and persistence of aquatic vegetation, aquatic system productivity and respiration, and other related ecological functions. Excessive fine sediment can degrade these functions through a range of processes including: (1) raising water temperatures by absorbing heat energy, (2) reducing light transmission through the water and decreasing photosynthesis by aquatic plants that affects dissolved oxygen concentrations, (3) burying channel substrate and spawning areas, and (4) decreasing the conveyance and storage capacity of stream networks as a result of excessive deposition in ponds and lakes (Kjelland and others, 2015). Fine-grained sedimentation on streambeds can also restrict benthic algal and macrophyte productivity and respiration (Yamada and Nakamura, 2002) where much of the productivity that supports the food web occurs; furthermore, decomposition of fine particulate organic matter may directly influence food webs and secondary productivity of consumers up through fish and mammal communities. Fine sediment also affects habitat quality for aquatic organisms that spend a portion of their life cycle in close contact with sediments,

Table D2. Drivers and indicators of fine sediment dynamics and related physicochemical controls of aquatic ecosystem health.

[Information is provided on constituents, drivers, indicators, and ancillary variables; relevance to aquatic ecosystem health; U.S. Environmental Protection Agency level of concern, benchmarks, and exceedances; general availability of U.S. Geological Survey (USGS) data for analysis; and key links and references. EPA, U.S. Environmental Protection Agency; 303(d), Clean Water Act Section 303(d); SSC, suspended sediment concentration; TSS, total suspended solids; O, oxygen; NWIS, USGS National Water Information System; FNU, Formazin Nephelometric Unit; NTU, Nephelometric Turbidity Unit; USGS NAWQA, National Water Quality Assessment; NRSA, EPA National Rivers and Streams Assessment; DNR, Department of Natural Resources; FPOM, fine particulate organic matter; OC, organic carbon; Q, streamflow; ADCP, acoustic Doppler current profiler; sed., sediment; %, percent; mg/L, milligrams per liter; mg/kg, milligram per kilogram; g/kg, gram per kilogram; mm, millimeters; wt, weight; <, less than; —, unavailable). USGS parameter codes available at https://help.waterdata.usgs.gov/codes-and-parameters/.]

Constituent, or indicator, or driver, or ancillary variable	Relevance to aquatic system health	Level of concern from EPA 303(d) listings of impaired waters	Benchmarks for aquatic life and level of exceedances	References
(SSC) and (TSS)[1]	Excess fine sediment causes loss of channel conveyance and reservoir storage capacity, facilitation of transport and storage of sorbed contaminants, burying of streambeds, consuming streambed O, and decreasing, direct interference with organism soft tissue and membranes, overall reduction in habitat quality.	EPA ranked fine sediment as 6th in number of nationally reported impairments; ranked 2nd as a "top 5" concern in 76% of large river basins.	Refer to Quality Criteria for Water, 1986 ("Gold Book") for narrative statistics.	Kuhnle and Simon, 2000; EPA, 1986 ("Gold Book"); EPA, 2017a, b, c.
Turbidity (FNU)[2]	Clouds water supply and may directly harm organism metabolic functions and feeding as well as reduce light availability for aquatic productivity, may indicate high levels of organics and microbial activity in water column that consume O and cause hypoxia.	EPA ranked turbidity as 11th in number of nationally reported impairments; ranked 8th as a "top 5" concern in 14% of large river basins.	FNU; NTU standard, like suspended sediment.	Joy and Jones, 2012.
Grain size of channel bed substrate[3]	Streambeds are critical habitat for macroinvertebrates such as aquatic insects and other infauna; growth substrate for benthic periphyton and algae and associated microbial colonies which provide a rich food source for particle feeding organisms in the food web. Also serves as a nursery area for fish eggs and early life stages of aquatic insects, refuge area during floods.	Many streams throughout the United States, over various contributing areas, geology, and land use.	Might have a D_{50} standard or threshold where impairment or mortality may occur, i.e., salmon spawning gravels.	Kaufmann and others, 2009; Riebe and others, 2014; Konrad and Gellis 2018; https://www.epa.gov/national-aquatic-resource-surveys/data-national-aquatic-resource-surveys; https://www.epa.gov/national-aquatic-resource-surveys/nrsa.
Organic content of sediment (mg/kg, g/kg, or mg/L)[4]	FPOM of the right amount and quality is critical to food webs however too much FPOM raises biological O demand and may cause hypoxia or anoxia.	—	—	—
Channel morphology	Sediment, flow, channel gradient; nutrient input, physical habitat.	Entire United States	Benthic organisms	Cluer and Thorne, 2014; Jowett, 1998; Newson and Newson, 2000. https://www.epa.gov/caddis-vol2/caddis-volume-2-sources-stressors-responses-physical-habitat

[1]Mass concentration of suspended sediment, TSS method biased toward finer fraction and organics.

[2]Measure of light scattering in water by suspended particles, plankton, and colored organic particles; directly estimates optical clarity and light availability, and is a useful surrogate for SSC.

[3]Summarized by metrics such as median grain size (D_{50}), percent fines (mass fraction <0.063 mm), and others; methods include sieving field samples or in situ pebble counts, measures of soft sediment area and depth, etc.

[4]Measured both in suspended sediment and in bed sediment.

using sediment as a substrate to cling to, for spawning, or as an escape from predation or as refugia from high temperatures and stormflow. Fine sediment deposition on streambeds particularly inhibits sensitive macroinvertebrate taxa (Burdon and others, 2013). In addition to altering food sources and processing by macroinvertebrates, fine sediment clogs membranes and causes physical damage in many fish species.

Sediment-Associated Transport of Constituents

Fine sediment may transport particle-associated constituents through streams and rivers to downstream receiving waters including lakes, reservoirs, and estuaries. The sediments can sequester and may later release to overlying water a variety of nutrients (phosphorus [P] and nitrogen [N]), toxic inorganic elements [metals, metalloids, radionuclides]), industrial chemicals (petrochemicals, polycyclic aromatic hydrocarbons [PAHs]), refractory pollutants (dichlorodiphenyltrichloroethane [DDT], polychlorinated biphenyl [PCB], chlorinated dioxins, plasticizers), and many emerging contaminants (pharmaceuticals, perfluorinated chemicals). Many of these chemicals sorb to sediment, although the degree of sorption can vary with sediment properties (such as grain size, surface area, mineralogy, carbon [C] content, and associated microbial biomass) and water quality parameters (such as pH, redox, salinity, and complexing agents). These chemicals can be stored on sediments in riverbeds, on banks and floodplains, or they may be transported with sediment (as suspended sediment in surface water, stormwater, into subsurface groundwater paths, or through aeolian processes).

Many toxic and bioaccumulated pollutants can be associated with fine sediments, often by sorption or precipitation, such as nutrients, metals, radionuclides, pesticides, PAHs, and other anthropogenic compounds (Foster and others, 2000; Horowitz and Stephens, 2008). Contaminants may be associated with sediments for long or short periods of time because the weak bonding to sediment coatings is often reversable with a change in redox, pH, or salinity, all of which may influence either the sorption capacities or the stability of the geochemical coatings on the sediments. In particular, the precipitation or dissolution behavior of iron (Fe) and manganese (Mn) oxyhydroxides is pH-dependent, which affects not only the dissolved metal concentrations but also the dynamics of many potentially toxic trace metals (mercury [Hg], arsenic [As], cadmium [Cd], aluminum [Al], copper [Cu], and so forth) as well as nutrients that sorb to metal or to organic coatings on sediment. For example, sediment-associated Hg varies with size and organic content of suspended matter (Skalak and Pizzuto, 2014). In addition, P and ammonium are often sorbed to sediments and may be transported with fine sediments that are mobilized by erosion of riverbeds and banks. In the Chesapeake Bay watershed, an average of 73 percent of total P and 18 percent of total N was transported to the estuary in a form attached to sediment (Zhang and others, 2015), with a higher percent of sediment-associated nutrients being supplied by tributaries with the highest sediment loads (Zhang and others, 2015).

Sediment-associated chemicals are of particular concern to benthic aquatic organisms when the chemicals have the potential to bioaccumulate and biomagnify (for example, DDT, Hg). Within the USGS Water Resources Mission Area (WMA), the Regional Stream Quality Assessment (RSQA) has assessed the importance of many of these sediment-associated contaminants to stream ecology (Rogers and others, 2016; Moran and others, 2017). The investigation of some of these chemicals in sediment cores from lakes and reservoirs has provided (1) information on contaminant trends, (2) an assessment of the effectiveness of management actions such as banning of chemicals, and (3) important forensic tools for sediment sourcing and dating (for example, Van Metre and Mahler, 2005). Historical records of sediment-associated metal releases from mines can be derived from sediment cores in reservoirs, such as the study by Blake and others (2020) in a drinking water reservoir in New Mexico. Thus, sediment records can be integrators of constituent loading and long-term changes of ecosystem health.

A key research area in sediment-associated contaminants deals with new and emerging contaminants such as perfluorinated chemicals, bifenthrin and other current-use hydrophobic pesticides. Whereas there has been substantial research and progress in understanding organochlorines, metals, and to some extent PAHs in sedimentary records (Van Metre and Fuller, 2009; Van Metre and Mahler, 2010), much work is left to be done on emerging contaminants. Perfluorinated chemicals are of high priority, because the distribution of these chemicals in the environment can be used to date and source sediment. In addition, the distribution of perfluorinated chemicals may provide information for similar (membrane and protein-associating) emerging contaminants. Sediment cores can record long-term inputs of per- and polyfluoroalkyl substances (PFAS) (Mussabek and others, 2019). An area of future research could examine existing archive material from USGS studies, focusing on WMA Integrated Water Science (IWS) basins where possible, and identify key places in IWS basins for possible follow-up work. This approach could benefit from building on existing dated material and ancillary data (a substantial cost in coring studies is the determination and interpretation of age models and ancillary data). Studies in contaminated urban sites could provide a good starting point for perfluorinated chemicals, as PAH and PFAS are commonly co-located. A second area of research could be to extrapolate and test the fidelity of chronology from previous studies (which may cover up to the 1990s) with modern coring efforts (Van Metre and Horowitz, 2013). This approach could also provide essential knowledge to determine if recent trends match previous trends, as well as the extent of alteration of previous trends through diagenesis. These approaches could provide connections between emerging contaminants in fine sediment and sedimentary records examined by other WMA efforts.

Sediment-associated nutrients have a role in legacy contamination and eutrophication of surface waters after they are released from sediments. Watershed P budgets have shown that P from eroding streambanks can contribute a substantial amount ranging from 6 to 93 percent of the total P load (Fox and others, 2016). In Lake Champlain, Vermont–New York, the total phosphorus contributions from eroding streambanks ranged from 6 to 30 percent (Ishee and others, 2015). In the Blue Earth River, Minnesota, streambanks contributed 7 to 10 percent of the phosphorus load with more than 90 percent of the phosphorus load originating from moderate and severely eroding sites (Sekely and others, 2002). In Chesapeake Bay, a total watershed mass balance for P indicated that 23 percent of all P sources (defined as streambank, upland sediment delivery to streams, and residual term) originated from streambanks (Noe and others, 2022). What is striking about these numbers is that the models and studies on P sources and trends have examined the land-surface applied P and not the contributions from streambank erosion. Phosphorus sources from within the river corridor also come from remobilization within ponds and reservoirs. In the Lower Susquehanna River of the Chesapeake Bay watershed, the three main reservoirs are approaching an equilibrium condition where the amount of phosphorus that settles with fine sediment is balanced by scouring during high flow events (Zhang and others, 2016).

Sorbed P and N that are released from sediments can become bioavailable and (or) cause algal blooms that may lead to fish kills. For example, changes in redox conditions can be the driver of P release, which can be affected by downstream widening, slowing, and blockage of river flow, which creates pooled waters that are deeper and have a longer residence time, while also having less mixing and reaeration of dissolved O across the water surface. Under such conditions, biogeochemical reactions such as aerobic respiration can consume much of the available O, causing anoxic conditions at sediment interfaces that promote the release of P from sediments. Desorption of P from sediments in small stormwater ponds is also an important source of P in the upstream channel network (Taguchi and others, 2020). Ammonium sequestration by fine sediment can be controlled by sorption to metal coatings that have precipitated on sediments. Release of adsorbed ammonium can therefore be controlled by redox conditions that affect Fe^{3+}/Fe^{2+} redox coupling or pH that may affect precipitation-dissolution kinetics.

Temporal changes in sediment-associated contamination in waterways have been studied by examining reservoir and lake cores to reveal an integrated contamination history of the inflowing streams and rivers. An important example are PAHs, which are a common contaminant in urban lakes and streams; cores from 40 lakes in urban areas across the United States indicate an increase in PAHs from the 1970s to 2000s with coal-tar based sealcoat being the largest source, followed by vehicle-related sources and coal combustion (Van Metre and Mahler, 2010). Sediment cores from 10 reservoirs and lakes in the United States indicated an association between PAHs and the amount of urban area in the basin (Van Metre and others, 2000) with PAH concentrations increasing over the last 20 to 40 years. The increased concentrations were associated with increasing combustion sources and with increased automobile use (Van Metre and Mahler, 2010; Van Metre and others, 2004). Sediment cores collected from 38 urban and reference lakes across the United States that were used to reconstruct water-quality histories, indicated downward trends in DDT and in dichlorodiphenyldichloroethylene (p,p′-DDE) concentrations, the main metabolite of DDT known to cause abnormalities in male sex development, and in total PCBs concentrations (Van Metre and Mahler, 2005). Upward and downward trends with time were observed for accumulation of chlordane, whereas trends in PAHs were mostly upward. However, it was noted that reservoir bottom-sediment samples might underestimate concentrations of organic contaminants in some streams (Van Metre and Mahler, 2004). In a recent study, a fine-particle breakdown of tire rubber, 6PPD-quinone, was found to be the answer to a decade-long search for the contaminant that poisons coho salmon (*Oncorhynchus kisutch*) after rainstorms in Puget Sound streams, and likely affects fish in urban waterways everywhere (Tian and others, 2021).

Many stream restorations projects focus on reducing fine sediment. Stream restoration projects that facilitate greater filtration of urban stream waters through soil and streambed sediment may be an effective management practice. Age-dated sediment cores could help prioritize regions of concern as a function of population density, stormwater infrastructure age, impervious surface, and other land use factors that inform model interpretations of water-quality trends at regional and national scales (Van Metre and others, 2004).

Managing Fine Sediment

When a river is determined to be impaired by sediment, it is placed on the EPA 303(d) list and a sediment TMDL may be implemented. Identifying sediment sources is an important step in the EPA's TMDL process (fig. D2), yet the States, Tribes, and local governments charged with this assessment and source tracking are often lacking standard guidance on appropriate tools available to quantify sediment sources and develop sediment budgets (Belmont and others, 2011; Gellis and others, 2016). Comprehensive data and models may be needed to assess fine sediment sources. A similar conclusion was reached in a review of sediment TMDLs in EPA Region IV (Southeast) in 2002 by the TMDL technical advisory group (TAG), a group composed of scientists from universities, Federal and State agencies, and non-governmental organizations (Keyes and Radcliffe, 2002). Two of the goals of the TAG were to identify general characteristics of scientifically based sediment TMDLs and to recommend a protocol for establishing sediment TMDLs in Georgia.

Recommendations by the TAG for sediment TMDL source assessment protocols, as described by Gellis and others (2016) included: (1) identify the problem based on currently available information, including water quality monitoring data, watershed analyses, information from the public, and any existing watershed studies; and (2) inventory the potential sediment sources and pathways by which sediment enters the waterbody, and thus obtain a robust quantification of the relative contribution from various sediment sources (emphasizing upland soil erosion or from channel corridor sources). The last recommendation highlights the fundamental question of whether sediment originates from upland soil erosion (for example, farmland, resource extraction, urban development) or channel bank erosion (Gellis and Walling, 2011), which can have substantial economic repercussions for stakeholders who must select whether to focus on stream restoration or soil conservation efforts.

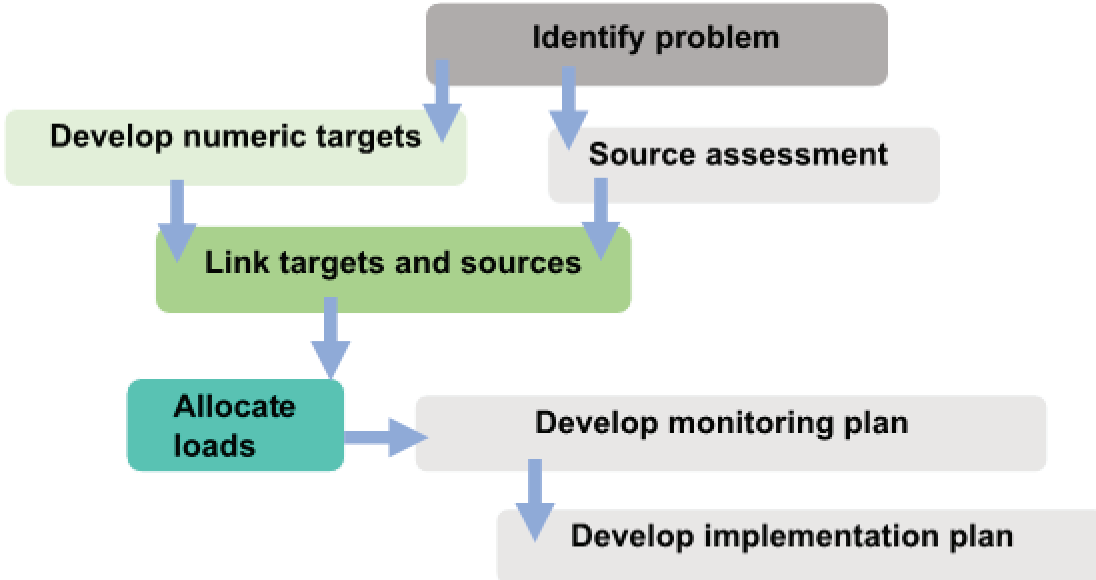


Figure D2. Flow diagram of the components in the sediment total maximum daily load (TMDL) procedure. Identifying sediment sources are important steps in the U.S. Environmental Protection Agency's (EPA) TMDL process. Modified from EPA, 1999.

Gaps in Fine Sediment Drivers and Associated Contaminants

Four principal knowledge gaps were introduced in the "Statement of the Problem" section of this chapter that limit our capabilities to predict fine-sediment impairment of ecological health:

1. Understanding fine sediment sources and connectivity through the Nation's waterways,
2. How fine sediment sources are apportioned between erosion in channel corridor versus uplands,
3. Predicting fine sediment-associated contaminants and biophysical drivers of eco-health, and
4. Ability to forecast climate and land-use driven alterations of fine sediment.

Information about sources, transport, and fate of fine sediment in streams throughout the Nation, implications for modeling sediment-associated contaminants and biophysical interactions affecting eco-health, and anticipating future changes driven by a changing climate and land use change (fig. D1) are important for enhancing the state of the science. Below we describe the four knowledge gaps in greater detail and begin to discuss how addressing gaps in fine sediment science can support stakeholders.

Gap 1. Understanding Fine Sediment Sources and Connectivity Through the Nation's Waterways

There is a gap in understanding the sources, transport, and fate of fine sediment (<0.063 mm; silts, clays, and fine particulate organic matter) in most river basins; only a few have been studied in detail. Sediment budgets quantify sediment dynamics from "source to sink" using data to estimate rates of erosion and export from other fine sediment sources to the fluvial system. Constructing a sediment budget requires compiling relevant data such as suspended sediment concentration and flux measurements and combining this information with estimates of fine sediment sources including soil and bank erosion, storage volumes and ages of sediment in channel margin, floodplain, and reservoir storage, and so forth. Computational tools such as fallout radionuclides are used to identify source areas and age-date the sediment. Extrapolation of metrics developed in well-studied cases are needed to model fine-sediment sources at scales ranging from small to medium watersheds (less than 250 square kilometers [km^2]) up to regional-sized river basins. Model output at a range of scales can inform stakeholders about the importance of landscape best-management practices (BMPs) versus stream restoration to mitigate negative outcomes. Models are used to answer questions such as, "Where is the majority of fine sediment originating from?" and "How long will it take for us to see the effects of upstream management actions on downstream outcomes that decrease the adverse effects of fine sediment?"

Gap 2. How Fine Sediment Sources are Apportioned Between Erosion in Channel Corridor Versus Uplands

A corollary of gap 1 is distinguishing sources of fine sediment from within the channel corridor versus from upland areas, including forest, agricultural, or urban areas. Identifying channel versus upland sources invokes totally different management strategies and thus it is imperative to distinguish. Source tracking methods combined with sediment budgets have been proven to partition channel versus upland sources. However, the field and laboratory work are expensive and time consuming, and thus there is a need for prioritizing key research areas that can eventually support model extrapolation throughout the Nation. Identifying source areas of excess fine sediment can provide the foundation for developing effective management strategies for stakeholders. Another key element of understanding sediment sources is determining the hydrologic pathways and sediment connectivity, over varying spatial and temporal scales, which occurs between the erosion, transport, storage, and delivery of sediment. Forecasting climate and land use changes also relies on this understanding.

Gap 3. Predicting Fine Sediment-Associated Contaminants and Biophysical Drivers of Eco-Health

Currently there is not a robust method to estimate the relative contributions of contaminants from streambank sources and how this compares with upland sources, in terms of their effect on sensitive aquatic systems. Yet, studies in a few areas have identified channel corridor processes as a dominant source of fine sediment and possibly also of certain associated contaminants (Fox and other, 2016; Noe and others, 2022). For example, bank erosion can be a source of fine sediment, as well as contaminant releases from sediments beneath slow-moving waters of ponds, wetlands, and reservoirs on the river network. Studies have shown that the mobilization of contaminants such as P from bank erosion, and from ponds and reservoirs, could be significant in the total watershed nutrient budget, yet wider spatial and temporal coverage is needed, not only for P but for a number of constituents of concern (OC, pesticides, heavy metals, and many anthropogenic contaminants). However, a full mass-balance of all sediment and P in these areas is needed to better define the sources of nutrients and other contaminants and determine the relative importance of stream bank erosion and upland sources.

Light attenuation caused by fine sediment has also been a driver of ecosystem degradation. Fine sediment which contains a high percentage of organic material can also increase O demand, which lowers O concentrations and degrades ecosystem habitat and food quality. Gaps exist in modeling fine sediment drivers of aquatic light availability and primary production, healthy O levels, and habitat quality as well as modeling particle-facilitated transport, storage, and remobilization of constituents. To be effective, modeling advancements need to be scalable and transferable to serve stakeholders wherever needed in the United States.

Gap 4. Ability to Forecast Climate and Land-Use Driven Alterations of Fine Sediment

Climate driven changes in precipitation and land use change influences flow regimes that will affect the erosion, delivery, and transport of watershed sediment sources as well as channel form and hydraulics. These changes, caused by changes in flow, in turn will redistribute loadings and mobilize new sources of fine sediment and associated contaminants. In turn, this may affect P loading, coastal sediment budgets, fine sediment colmation of streambeds, and biological O demand. Changes in climate and land-use together are likely to affect fine sediment dynamics throughout the Nation's fluvial system for a broad range of land uses whether forested, cultivated, or urbanized. These potential changes lead to a few questions. Will increased drought and wildfires (and associated debris flows) in the western United States increase sediment loads, turbidity and biological O demand, channel aggradation, and flooding? For example, in the western United States, longer wildfire seasons and hotter fires are altering soil integrity by increasing hydrophobicity and erodibility and are expected to increase loading of fine sediment with a high black C content and biological O demand to streams under post-wildfire conditions (Wagner and others, 2015). In the northeastern United States, where a wetter and warmer climate is predicted (Rustad and others, 2012), will channel morphology and sediment-associated loadings of nutrients adjust in ways that exacerbate large river and estuarine algal blooms? For the management community to prepare for the future, an adaptive modeling capacity is needed along with well-conceived scenarios to bracket a range of potential future drivers.

Addressing Gaps—Approaches and Priorities

A summary of fine sediment gaps, including background and rationale and measurements, metrics, and modeling approaches, as well as key references is provided in table D1. Gaps are listed individually but each of the gaps is not isolated from the other gaps; rather most of the gaps are interdependent.

Tracing Sediment Sources

An understanding of the source-to-sink dynamics of fine sediment is needed to improve predictive capabilities (fig. D1). A source-to-sink characterization involves sediment source type, erosion, delivery, transport, and storage controls, all of which can benefit from the use of tracers to identify sources. Recent advances in using the geochemical properties (sediment fingerprinting), to trace sediment source areas and ages vastly improved calculating sediment budgets by providing a direct, quantitative estimate of the source contributions of fine sediment (Gellis and Walling, 2011; Gellis and others, 2016; Collins and others, 2020). This approach entails the identification of specific sources of sediment through the establishment of a minimal set of physical and (or) chemical properties, that is, tracers that uniquely define each source in the watershed. Fine sediments collected under different flow conditions exhibit a composite, or fingerprint of properties that allows them to be traced back to their respective sources. Tracers that have successfully been used in the sediment-fingerprinting approach include color (Martínez-Carreras and others, 2010; Barthod and others, 2015), grain size (Kurashige and Fusejima, 1997; Weltje and Prins, 2007); organic matter fluorescence (Larsen and others, 2015), signatures clay mineralogy (Eberl, 2004; Gingele and De Deckker, 2005), mineral-magnetism (Zhang and others, 2008; Maher and others, 2009), geochemistry (Gellis and Gorman Sanisaca, 2018), fallout radionuclides (Belmont and others, 2014; Evrard and others, 2016; Gellis and others, 2017), bulk stable isotopes and isotopic ratios (Fox and Papanicolaou, 2008), and biomarkers and biologic properties (Hancock and Revill, 2013; Alewell and others, 2016; Reiffarth and others, 2016). Sediment in channel storage on the bed of the channel (drape or interstitial) can be an important source of sediment. However, this sediment is derived from upstream sources (bed, banks, and uplands) and is a mixture of geochemical concentrations from these sources and may not have a unique fingerprint. However, recent work using microbial DNA indicates that source material can have a unique assemblage of bacteria and DNA (Zhang and others, 2016; Evrard and others, 2019). Thus, we identify that sediment deposited on the bed of the channel is a ”knowledge gap” in sediment fingerprinting science. The use of DNA to fingerprint bed sediment could be further examined.

Fallout radionuclides (FRN) (excess lead-210 [$^{210}Pb_{ex}$] and beryllium-7 [^{7}Be]) were used in the RSQA–NAWQA (National Water Quality Assessment) program to determine the sources of sediment (upland versus channel) for large regions of the United States (Gellis and others, 2017). Excess ^{210}Pb and ^{7}Be FRNs can also be used to date fluvial sediment (^{7}Be to one year and $^{210}Pb_{ex}$ to approximately 100 years). The age of sediment can inform managers of the timescales when BMPs may show an effect. If sediment ages are estimated to be relatively young (that is, a few years or less), then monitoring programs may be expected to show a relatively quick decrease in sediment related to specific management actions that target those sources. If sediment is older (that is, decades), then it is likely to take longer to see a reduction in sediment concentrations and loads. Combining sediment-source analysis with age dating can provide modelers with data needed to predict sources and outcomes that will help inform managers about effective means of control.

For modeling sediment, it has been proposed to collect bed sediment at monitoring stations in each USGS WMA study basin to determine the sources and ages of sediment. Sediment sources and sediment ages could be estimated through development of a regional sediment model for the proposed USGS large regional areas (such as the Delaware River Basin, Upper Colorado River Basin, and Illinois River Basin). The proposed statistical model could build upon existing models developed for the Delaware River Basin (Noe and others, 2020b; https://www2.usgs.gov/water/southatlantic/projects/floodplains/) which used data from field collection at 15 monitoring sites and the Floodplain and Channel Evaluation Tool (FACET, https://www.usgs.gov/software/floodplain-and-channel-evaluation-tool-facet). Dendrochronology, field surveying, and sediment physio-chemistry were used to calculate changes in floodplain deposition and streambank erosion over time to create a quasi-sediment budget for each site. FACET incorporates high resolution airborne lidar to estimate channel morphology, and along with characteristics of the upstream drainage area, was used to extrapolate the monitoring station results for large river basins. Statistical analysis which included random forest regression was used to develop statistical models of sediment flux with predictions of floodplain and streambank flux for each National Hydrography Dataset Plus version 2 (NHDPlusV2) reach (https://www.epa.gov/waterdata/get-nhdplus-national-hydrography-dataset-plus-data).

Modeling Fine Sediment Dynamics and Associated Contaminants

Sources of excess N or P may be from sources mobilized in the present season, or they may be from “legacy sources” where nutrients were stored in soils, groundwaters, or in river or reservoir sediments for several seasons, years, or decades before being released and transported to receiving waters. Commonly used water quality models do not typically quantify “legacy sources” of sediment-associated nutrients or characterize the key controls and their associated lag times, and therefore these models may overlook key dynamic processes that may trigger adverse effects such as hypoxia and anoxia and harmful algal blooms (HABs). Nutrients transported with sediments and later released to the water column can exacerbate these conditions. Conservation practices may affect legacy sources differently than contemporary sources or take longer to be effective. Modeling of legacy nutrient sources beyond the reach of conservation practices has high potential to improve management strategies.

Among the predictive models that have been applied everywhere in the Nation are the USGS SPARROW sediment models (Brakebill and others, 2010; Robertson and Saad, 2019) as well as sediment-trend analysis (Murphy, 2020). However, these approaches tend to not separate terrestrial topsoil erosion sources from channel corridor erosion sources, which all require different management strategies. For example, recent studies indicate that streambanks may not only be an important source but the dominant source of sediment in many areas (Noe and others, 2020a). In addition, studies in the Midwestern United States, Lake Champlain in Vermont, and Chesapeake Bay indicate that eroding streambanks also contain high levels of N and P, and possibly other contaminants (pesticides, insecticides, and PAHs) (Sekely and others, 2002; Schilling and others, 2009; Ishee and others, 2015).

Extended model capabilities are needed that provide:

- Statistically based and physics guided model structure (for example, SPARROW or similar) with spatial referencing of flow and transport parameters (for example, Schmadel and others, 2019);

- Dynamically enabled model structure that specifies both sources and sinks for fine sediment and constituents in the channel corridor;

- Input predictors that help identify sources, timing, and causes of excess nutrient deliveries to receiving waters, including legacy contributions, that fuel hypoxia and HABs; and

- Seasonal to decadal, scenario-based load projections to help prioritize the most effective mitigation strategies.

These new modeling strategies could help build communities of collaborators to address the grand challenge of hypoxia and HABs with new science that improves control efforts and informs new styles of management (for example, nutrient trading).

There are additional gaps in understanding fine sediment that could help address how the fluvial system could respond to climate change. Climate driven changes in flow regime could affect hydraulics and suspended sediment loads in ways that affect nutrient loading, coastal sediment budgets, fine sediment colmation of streambeds, biological oxygen demand, and others. The effects of climate change are uncertain. For example, how and where will flows change in a wetter and warmer eastern United States to affect the sediment regime? In the American west, will increasing drought and wildfires (and associated debris flows) lead to channel aggradation and flooding? Concomitantly, how and where in the watershed will climate change affect sediment sources? Lastly, how long will it take to adjust management actions to reduce sediment fluxes?

Furthermore, the USGS and its partners still do not have a robust method to estimate streambank erosion nor quantify the contributions of sediment, nutrients, and contaminants from streambank erosion. How can fine sediment from channel storage (bed material) be traced? The USGS WMA has an opportunity to develop measurement tools and modeling techniques to estimate the relative importance of streambank erosion to other sources, as well as to account for how those sources change over time along with changing channel morphology and hydroclimatic drivers.

Timelines

Near-Term (2 Years)

Within two years, the WMA could develop a proof-of-concept approach to developing a sediment budget for one of the WMA IWS basins and surrounding regional drainage basins. The focus of the sediment budget would be on sediment-source and sediment flux characterization, with modeling informed by already published and ongoing studies of upland and channel bank sediment sources, channel and floodplain fluxes, turbidity as a surrogate for fluxes, and sediment age determinations. Ideally there could be investigations using sediment sourcing and sediment age dating using fallout radionuclides (^{7}Be, ^{210}Pb$_{ex}$, cesium-137 [^{137}Cs]), as well as upland sediment modelling using the revised universal soil loss equation (RUSLE, https://www.ars.usda.gov/southeast-area/oxford-ms/national-sedimentation-laboratory/watershed-physical-processes-research/docs/revised-universal-soil-loss-equation-rusle-welcome-to-rusle-1-and-rusle-2/) or similar with remapped soil properties (for example, Chaney and others, 2019; Woznicki and others, 2020) combined with a digital elevation model (DEM) connectivity-model tracking channel and floodplain fluxes using the FACET model or similar tools. Products could include: (1) sediment budget storyboard showing how fine sediment is transferred from source to sink; (2) proof-of-concept of a method to distinguish uplands and channel bed as a sediment source; and (3) time-averaged (seasonal or monthly) statistical model of sediment sources and fluxes for one or more WMA IWS basins and the surrounding regional drainage basin.

Mid-Term (2–5 Years)

Within 5 years, the WMA could expand into additional IWS basins and their regional drainage basins with statistical models describing sediment sources and sediment fluxes. Statistical analysis could be expanded to include random forest regression or other statistical approaches (such as enhanced SPARROW models) to develop statistical models of sediment flux with predictions of floodplain and streambank flux for each NHDPlusV2 reach. Comparisons could also be made between existing USGS models and other models, that is, regional SPARROW models compared with Soil and Water Assessment Tool (SWAT) models (https://swat.tamu.edu/) where predictions from one model at a single scale could be incorporated as predictors in another model at a different scale. For example, SWAT has more process-related variables, but it also has greater requirements for data inputs; therefore, SWAT tends to be typically used only in small watersheds. Comparing SWAT results with SPARROW estimations from larger basins could improve the scaling capacity of SWAT and the process basis in SPARROW. The result may provide a scalable, process-guided statistical model of sediment sources and fluxes that could be widely applicable throughout the United States. Products from these type of efforts may include: (1) enhanced sediment budget storyboarding of how fine sediment is transferred from source to sink; (2) scalable process-guided statistical models of sediment sources; (3) sediment fluxes for multiple IWS basins and surrounding regional drainage basins; and (4) inter-agency interactions in sediment modeling, for example SPARROW-SWAT comparisons, to build process modeling skill of regional-scale statistical models could lead to further interactions between the USGS and the U.S. Department of Agriculture (USDA).

Long-Term (10 Years)

A long-range plan could be develop a national model of sediment sourcing and fluxes that includes floodplain, ponded water, and streambank erosion-deposition fluxes. By incorporating results from IWS basins (Delaware River Basin, Upper Colorado River Basin, Illinois River Basin, and future basins), we could obtain the fluvial sediment flux estimates and streambank and floodplain fluxes necessary for a model. FACET, random forest (a machine learning algorithm), and SPARROW models could be used to improve the accuracy, timeliness, and spatial extent of improved sediment flux estimates and sources in unmonitored areas across the country. This sediment information could then be used directly by resource managers and be incorporated into regional or national models to improve estimates of sediment flux which in many areas is important in describing water availability from water-supply sedimentation and turbidity. Products include: (1) National model of sediment sources, fluxes, and ages that is process guided and can therefore predict future conditions based on scenarios of land-use and climate change; and (2) full sediment budget storyboard of how fine sediment is transferred from source to sink.

References Cited

Alewell, C., Birkholz, A., Meusburger, K., Schindler Wildhaber, Y., and Mabit, L., 2016, Quantitative sediment source attribution with compound-specific isotope analysis in a C3 plant-dominated catchment (central Switzerland): Biogeosciences, v. 13, no. 5, p. 1587–1596, https://doi.org/10.5194/bg-13-1587-2016.

Asselman, N.E.M., 1995, The impact of climate change on suspended sediment transport in the river Rhine, *in* Zwerver, S., van Rompaey, R.S.A.R., Kok, M.T.J., and Berk, M.M., eds., Climate change research—Evaluation and policy implications, International climate change research conference, Maastricht, The Netherlands, December 6–9, 1994, Proceedings: Studies in Environmental Science, v. 65, p. 937–942, https://doi.org/10.1016/S0166-1116(06)80119-6.

Barthod, L.R.M., Liu, K., Lobb, D.A., Owens, P.N., Martínez-Carreras, N., Koiter, A.J., Petticrew, E.L., McCullough, G.K., Liu, C., and Gaspar, L., 2015, Selecting color-based tracers and classifying sediment sources in the assessment of sediment dynamics using sediment source fingerprinting: Journal of Environmental Quality, v. 44, no. 5, p. 1605–1616, accessed mm dd, yyyy, at https://doi.org/10.2134/jeq2015.01.0043.

Belmont, P., Gran, K.B., Schottler, S.P., Wilcock, P.R., Day, S.S., Jennings, C., Lauer, J.W., Viparelli, E., Willenbring, J.K., Engstrom, D.R., and Parker, G., 2011, Large shift in source of fine sediment in the Upper Mississippi River: Environmental Science & Technology, v. 45, no. 20, p. 8804–8810, https://doi.org/10.1021/es2019109.

Belmont, P., Willenbring, J.K., Schottler, S.P., Marquard, J., Kumarasamy, K., and Hemmis, J.M., 2014, Toward generalizable sediment fingerprinting with tracers that are conservative and nonconservative over sediment routing timescales: Journal of Soils and Sediments, v. 14, no. 8, p. 1479–1492, https://doi.org/10.1007/s11368-014-0913-5.

Bernhardt, E.S., Heffernan, J.B., Grimm, N.B., Stanley, E.H., Harvey, J.W., Arroita, M., Appling, A.P., Cohen, M.J., McDowell, W.H., Hall, R.O., Jr., Read, J.S., Roberts, B.J., Stets, E.G., and Yackulic, C.B., 2018, The metabolic regimes of flowing waters: Limnology and Oceanography, v. 63, no. S1, p. S99–S118, https://doi.org/10.1002/lno.10726.

Berry, W., Rubinstein, N., Melzian, B., and Hill, B., 2003, The biological effects of suspended and bedded sediment (SABS) in aquatic systems—A Review: U.S. Environmental Protection Agency, appendix 1, 58 p., accessed November 1, 2021, at https://archive.epa.gov/epa/sites/production/files/2015-10/documents/sediment-appendix1.pdf.

Blake, J.M., Brown, J.E., Ferguson, C.L., Bixby, R.J., and Delay, N.T., 2020, Sediment record of mining legacy and water quality from a drinking-water reservoir, Aztec, New Mexico, USA: Environmental Earth Sciences, v. 79, no. 17, article 404, 21 p., https://doi.org/10.1007/s12665-020-09126-9.

Borselli, L., Cassi, P., and Torri, D., 2008, Prolegomena to sediment and flow connectivity in the landscape—A GIS and field numerical assessment: CATENA, v. 75, no. 3, p. 268–277, https://doi.org/10.1016/j.catena.2008.07.006.

Bracken, L.J., Turnbull, L., Wainwright, J., and Bogaart, P., 2015, Sediment connectivity—A framework for understanding sediment transfer at multiple scales: Earth Surface Processes and Landforms, v. 40, no. 2, p. 177–188, https://doi.org/10.1002/esp.3635.

Brakebill, J.W., Ator, S.W., and Schwarz, G.E., 2010, Sources of suspended-sediment flux in streams of the Chesapeake Bay watershed—A regional application of the SPARROW model: Journal of the American Water Resources Association, v. 46, no. 4, p. 757–776, https://doi.org/10.1111/j.1752-1688.2010.00450.x.

Burdon, F.J., McIntosh, A.R., and Harding, J.S., 2013, Habitat loss drives threshold response of benthic invertebrate communities to deposited sediment in agricultural streams: Ecological Applications, v. 23, no. 5, p. 1036–1047, https://doi.org/10.1890/12-1190.1.

Bussi, G., Darby, S.E., Whitehead, P.G., Jin, L., Dadson, S.J., Voepel, H.E., Vasilopoulos, G., Hackney, C.R., Hutton, C., Berchoux, T., Parsons, D.R., and Nicholas, A., 2021, Impact of dams and climate change on suspended sediment flux to the Mekong delta: Science of the Total Environment, v. 755, part 1, article 142468, 12 p., at https://doi.org/10.1016/j.scitotenv.2020.142468.

Chaney, N.W., Minasny, B., Herman, J.D., Nauman, T.W., Brungard, C.W., Morgan, C.L.S., McBratney, A.B., Wood, E.F., and Yimam, Y., 2019, POLARIS soil properties—30-m probabilistic maps of soil properties over the contiguous United States: Water Resources Research, v. 55, no. 4, p. 2916–2938, https://doi.org/10.1029/2018WR022797.

Cluer, B. and Thorne, C., 2014, A stream evolution model integrating habitat and ecosystem benefits: River Research and Applications, v. 30, no. 2, p. 135–154, https://doi.org/10.1002/rra.2631.

Collins, A.L., Blackwell, M., Boeckx, P., Chivers, C.-A., Emelko, M., Evrard, O., Foster, I., Gellis, A., Gholami, H., Granger, S., Harris, P., Horowitz, A.J., Laceby, J.P., Martinez-Carreras, N., Minella, J., Mol, L., Nosrati, K., Pulley, S., Silins, U., da Silva, Y.J., Stone, M., Tiecher, T., Upadhayay, H.R., and Zhang, Y., 2020, Sediment source fingerprinting: benchmarking recent outputs, remaining challenges and emerging themes: Journal of Soils and Sediments, v. 20, no. 12, p. 4160–4193, https://doi.org/10.1007/s11368-020-02755-4.

Collins, A.L., Pulley, S., Foster, I.D.L., Gellis, A., Porto, P., and Horowitz, A.J., 2017, Sediment source fingerprinting as an aid to catchment management—A review of the current state of knowledge and a methodological decision-tree for end-users: Journal of Environmental Management, v. 194, special issue, p. 86–108, https://doi.org/10.1016/j.jenvman.2016.09.075.

Crema, S., and Cavalli, M., 2018, SedInConnect—A stand-alone, free and open source tool for the assessment of sediment connectivity: Computers & Geosciences, v. 111, p. 39–45, https://doi.org/10.1016/j.cageo.2017.10.009.

Eberl, D.D., 2004, Quantitative mineralogy of the Yukon River system—Changes with reach and season, and determining sediment provenance: American Mineralogist, v. 89, nos. 11–12, p. 1784–1794, https://doi.org/10.2138/am-2004-11-1225.

Evrard, O., Laceby, J.P., Ficetola, G.F., Gielly, L., Huon, S., Lefèvre, I., Onda, Y., and Poulenard, J., 2019, Environmental DNA provides information on sediment sources—A study in catchments affected by Fukushima radioactive fallout: Science of the Total Environment, v. 665, p. 873–881, https://doi.org/10.1016/j.scitotenv.2019.02.191.

Evrard, O., Laceby, J.P., Huon, S., Lefèvre, I., Sengtaheuanghoung, O., and Ribolzi, O., 2016, Combining multiple fallout radionuclides (^{137}Cs, ^{7}Be, ^{210}Pb$_{xs}$) to investigate temporal sediment source dynamics in tropical, ephemeral riverine systems: Journal of Soils and Sediments, v. 16, no. 3, p. 1130–1144, https://doi.org/10.1007/s11368-015-1316-y.

Foster, G.D., Roberts, E.C., Gruessner, B., and Velinsky, D.J., 2000, Hydrogeochemistry and transport of organic contaminants in an urban watershed of Chesapeake Bay (USA): Applied Geochemistry, v. 15, no. 7, p. 901–915, https://doi.org/10.1016/S0883-2927(99)00107-9.

Fox, J.F., and Papanicolaou, A.N., 2008, Application of the spatial distribution of nitrogen stable isotopes for sediment tracing at the watershed scale: Journal of Hydrology, v. 358, no. 1, p. 46–55, https://doi.org/10.1016/j.jhydrol.2008.05.032.

Fox, G.A., Purvis, R.A., and Penn, C.J., 2016, Streambanks—A net source of sediment and phosphorus to streams and rivers: Journal of Environmental Management, v. 181, p. 602–614, https://doi.org/10.1016/j.jenvman.2016.06.071.

Gellis, A.C., Fitzpatrick, F.A., and Schubauer-Berigan, J., 2016, A manual to identify sources of fluvial sediment: U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Land Remediation and Pollution Control Division, no. EPA/600/R-16/210, 106 p. accessed November 1, 2021, at https://nepis.epa.gov/Exe/ZyPDF.cgi/P100QVM1.PDF?Dockey=P100QVM1.PDF.

Gellis, A.C., Fuller, C.C., and Van Metre, P.C., 2017, Sources and ages of fine-grained sediment to streams using fallout radionuclides in the Midwestern United States: Journal of Environmental Management, v. 194, p. 73–85, https://doi.org/10.1016/j.jenvman.2016.06.018.

Gellis, A.C., Fuller, C.C., Van Metre, P., Filstrup, C.T., Tomer, M.D., Cole, K.J., and Sabitov, T.Y., 2019, Combining sediment fingerprinting with age-dating sediment using fallout radionuclides for an agricultural stream, Walnut Creek, Iowa, USA: Journal of Soils and Sediments, v. 19, no. 9, p. 3374–3396, https://doi.org/10.1007/s11368-018-2168-z.

Gellis, A.C., Fuller, C.C., Van Metre, P.C., Mahler, B.J., Welty, C., Miller, A.J., Nibert, L.A., Clifton, Z.J., Malen, J.J., and Kemper, J.T., 2020, Pavement alters delivery of sediment and fallout radionuclides to urban streams: Journal of Hydrology, v. 588, article 124855, 13 p., https://doi.org/10.1016/j.jhydrol.2020.124855.

Gellis, A.C., and Gorman Sanisaca, L., 2018, Sediment fingerprinting to delineate sources of sediment in the agricultural and forested Smith Creek watershed, Virginia, USA: Journal of the American Water Resources Association, v. 54, no. 6, p. 1197–1221, https://doi.org/10.1111/1752-1688.12680.

Gingele, F.X., and De Deckker, P., 2005, Clay mineral, geochemical and Sr–Nd isotopic fingerprinting of sediments in the Murray–Darling fluvial system, southeast Australia: Australian Journal of Earth Sciences, v. 52, no. 6, p. 965–974, https://doi.org/10.1080/08120090500302301.

Hancock, G.J., and Revill, A.T., 2013, Erosion source discrimination in a rural Australian catchment using compound-specific isotope analysis (CSIA): Hydrological Processes, v. 27, no. 6, p. 923–932, at https://doi.org/10.1002/hyp.9466.

Horowitz, A.J., and Stephens, V.C., 2008, The effects of land use on fluvial sediment chemistry for the conterminous U.S.—Results from the first cycle of the NAWQA Program—Trace and major elements, phosphorus, carbon, and sulfur: Science of the Total Environment, v. 400, nos. 1–3, p. 290–314, https://doi.org/10.1016/j.scitotenv.2008.04.027.

Ishee, E.R., Ross, D.S., Garvey, K.M., Bourgault, R.R., and Ford, C.R., 2015, Phosphorus characterization and contribution from eroding streambank soils of Vermont's Lake Champlain Basin: Journal of Environmental Quality, v. 44, no. 6, p. 1745–1753, https://doi.org/10.2134/jeq2015.02.0108.

Jones, J.I., Murphy, J.F., Collins, A.L., Sear, D.A., Naden, P.S., and Armitage, P.D., 2012, The impact of fine sediment on macro-invertebrates: River Research and Applications, v. 28, no. 8, p. 1055–1071, https://doi.org/10.1002/rra.1516.

Joy J., and Jones, J., 2012, Little Spokane River watershed fecal coliform bacteria, temperature, and turbidity total maximum daily load: Washington State Department of Ecology, Water Quality Improvement Report, no. 11-10-075, 256 p., accessed November 1, 2021, at https://apps.ecology.wa.gov/publications/documents/1110075.pdf.

Jowett, I.G., 1998, Hydraulic geometry of New Zealand rivers and its use as a preliminary method of habitat assessment Regulated Rivers—Research & Management, v. 14, no. 5, p. 451–466, https://doi.org/10.1002/(SICI)1099-1646(1998090)14:5%3C451::AID-RRR512%3E3.0.CO;2-1.

Karwan, D.L., Pizzuto, J.E., Aalto, R., Marquard, J., Harpold, A., Skalak, K., Benthem, A., Levia, D.F., Siegert, C.M., and Aufdenkampe, A.K., 2018, Direct channel precipitation and storm characteristics influence short-term fallout radionuclide assessment of sediment source: Water Resources Research, v. 54, no. 7, p. 4579–4594, https://doi.org/10.1029/2017WR021684.

Kaufmann, P.R., Larsen, D.P., and Faustini, J.M., 2009, Bed stability and sedimentation associated with human disturbances in Pacific Northwest streams: Journal of the American Water Resources Association, v. 45, no. 2, p. 434–459, https://doi.org/10.1111/j.1752-1688.2009.00301.x.

Keyes, A.M., and Radcliffe, D., 2002, A protocol for establishing sediment TMDLs: Atlanta, Georgia Conservancy and University of Georgia Institute of Ecology prepared by Sediment TDML Technical Advisory Group, 31 p., accessed November 1, 2021, at https://rivercenter.uga.edu/wp-content/uploads/2021/01/A-Protocol-for-Establishing-Sediment-TMDLs.pdf.

Kjelland, M.E., Woodley, C.M., Swannack, T.M., and Smith, D.L., 2015, A review of the potential effects of suspended sediment on fishes—Potential dredging-related physiological, behavioral, and transgenerational implications: Environment Systems and Decisions, v. 35, no. 3, p. 334–350, at https://doi.org/10.1007/s10669-015-9557-2.

Kondolf, G.M., Gao, Y., Annandale, G.W., Morris, G.L., Jiang, E., Zhang, J., Cao, Y., Carling, P., Fu, K., Guo, Q., Hotchkiss, R., Peteuil, C., Sumi, T., Wang, H.-W., Wang, Z., Wei, Z., Wu, B., Wu, C., and Yang, C.T., 2014, Sustainable sediment management in reservoirs and regulated rivers—Experiences from five continents: Earth's Future, v. 2, no. 5, p. 256–280, https://doi.org/10.1002/2013EF000184.

Konrad, C. and Gellis, A., 2018, Factors influencing fine sediment on stream beds in the midwestern United States: Journal of Environmental Quality, v. 47, no. 5, p. 1214–1222, https://doi.org/10.2134/jeq2018.02.0060.

Kuhnle, R.A., and Simon, A., 2000, Evaluation of sediment transport data for clean sediment TMDLs: U.S. Department of Agriculture, Agricultural Research Service, National Sedimentation Laboratory NSL Report no. 17, 62 p., accessed November 1, 2021, at https://www.ars.usda.gov/ARSUserFiles/60600505/PDF/NSLReport17.pdf.

Kurashige, Y., and Fusejima, Y., 1997, Source identification of suspended sediment from grain-size distributions, I—Application of nonparametric statistical tests: CATENA, v. 31, nos. 1–2, p. 39–52, https://doi.org/10.1016/S0341-8162(97)00033-7.

Larsen, M.C., Gellis, A.C., Glysson, G.D., Gray, J.R., and Horowitz, A.J., 2010, Fluvial sediment in the environment—A national challenge, *in* 4th Federal Interagency Hydrologic Modeling Conference and the 9th Federal Interagency Sedimentation Conference, Hydrology and Sedimentation for a Changing Future Existing and Emerging Issues, Las Vegas, June 27–July 1, 2010, Proceedings: Advisory Committee on Water Information (ACWI), 14 p., accessed November 1, 2021 at https://acwi.gov/sos/pubs/2ndJFIC/Contents/OS_Larsen_9fisc_sediment_vision_3_4_2010.pdf.

Larsen, L., Harvey, J., Skalak, K., and Goodman, M., 2015, Fluorescence-based source tracking of organic sediment in restored and unrestored urban streams: Limnology and Oceanography, v. 60, no. 4, p. 1439–1461, https://doi.org/10.1002/lno.10108.

Maher, B.A., Watkins, S.J., Brunskill, G., Alexander, J., and Fielding, C.R., 2009, Sediment provenance in a tropical fluvial and marine context by magnetic 'fingerprinting' of transportable sand fractions: Sedimentology, v. 56, no. 3, p. 841–861, at https://doi.org/10.1111/j.1365-3091.2008.00999.x.

Martínez-Carreras, N., Udelhoven, T., Krein, A., Gallart, F., Iffly, J.F., Ziebel, J., Hoffmann, L., Pfister, L., and Walling, D.E., 2010, The use of sediment colour measured by diffuse reflectance spectrometry to determine sediment sources—Application to the Attert River catchment (Luxembourg): Journal of Hydrology, v. 382, no. 1, p. 49–63, https://doi.org/10.1016/j.jhydrol.2009.12.017.

Moragoda, N., and Cohen, S., 2020, Climate-induced trends in global riverine water discharge and suspended sediment dynamics in the 21st century: Global and Planetary Change, v. 191, article 103199, 13 p., https://doi.org/10.1016/j.gloplacha.2020.103199.

Moran, P.W., Nowell, L.H., Kemble, N.E., Mahler, B.J., Waite, I.R., and Van Metre, P.C., 2017, Influence of sediment chemistry and sediment toxicity on macroinvertebrate communities across 99 wadable streams of the Midwestern USA: Science of the Total Environment, v. 599–600, p. 1469–1478, https://doi.org/10.1016/j.scitotenv.2017.05.035.

Mukundan, R., Walling, D.E., Gellis, A.C., Slattery, M.C., and Radcliffe, D.E., 2012, Sediment source fingerprinting—Transforming from a research tool to a management Tool: Journal of the American Water Resources Association, v. 48, no. 6, p. 1241–1257, https://doi.org/10.1111/j.1752-1688.2012.00685.x.

Murphy, J.C., 2020, Changing suspended sediment in United States rivers and streams—Linking sediment trends to changes in land use/cover, hydrology and climate: Hydrology and Earth System Sciences, v. 24, no. 2, p. 991–1010, https://doi.org/10.5194/hess-24-991-2020.

Mussabek, D., Ahrens, L., Persson, K.M., and Berndtsson, R., 2019, Temporal trends and sediment–water partitioning of per- and polyfluoroalkyl substances (PFAS) in lake sediment: Chemosphere, v. 227, p. 624–629, https://doi.org/10.1016/j.chemosphere.2019.04.074.

Newson, M.D., and Newson, C.L., 2000, Geomorphology, ecology and river channel habitat—Mesoscale approaches to basin-scale challenges: Progress in Physical Geography—Earth and Environment, v. 24, no. 2, p. 195–217, https://doi.org/10.1177/030913330002400203.

Noe, G.B., Cashman, M.J., Skalak, K., Gellis, A., Hopkins, K.G., Moyer, D., Webber, J., Benthem, A., Maloney, K., Brakebill, J., Sekellick, A., Langland, M., Zhang, Q., Shenk, G., Keisman, J., and Hupp, C., 2020a, Sediment dynamics and implications for management—State of the science from long-term research in the Chesapeake Bay watershed, USA: WIREs Water, v. 7, no. 4, article e1454, 28 p., https://doi.org/10.1002/wat2.1454.

Noe, G. B., Hopkins, K. G., Claggett, P. R., Schenk, E. R., Metes, M. J., Ahmed, L., Doody, T.R., and Hupp, C. R., 2022, Streambank and floodplain geomorphic change and contribution to watershed material budgets: Environmental Research Letters, v. 17, no. 6, https://doi.org/10.1088/1748-9326/ac6e47.

Noe, G.B., Hupp, C.R., Schenk, E.R., Doody, T.R., and Hopkins, K.G., 2020b, Physico-chemical characteristics and sediment and nutrient fluxes of floodplains, streambanks, and streambeds in the Chesapeake Bay and Delaware River watersheds: U.S. Geological Survey data release, https://doi.org/10.5066/P9QLJYPX.

Owens, P.N., Batalla, R.J., Collins, A.J., Gomez, B., Hicks, D.M., Horowitz, A.J., Kondolf, G.M., Marden, M., Page, M.J., Peacock, D.H., Petticrew, E.L., Salomons, W., and Trustrum, N.A., 2005, Fine-grained sediment in river systems—Environmental significance and management issues: River Research and Applications, v. 21, no. 7, p. 693–717, https://doi.org/10.1002/rra.878.

Riebe, C.S., Sklar, L.S., Overstreet, B.T. and Wooster, J.K., 2014, Optimal reproduction in salmon spawning substrates linked to grain size and fish length: Water Resources Research, v. 50, no. 2, p. 898–918, https://doi.org/10.1002/2013WR014231.

Reiffarth, D.G., Petticrew, E.L., Owens, P.N., and Lobb, D.A., 2016, Sources of variability in fatty acid (FA) biomarkers in the application of compound-specific stable isotopes (CSSIs) to soil and sediment fingerprinting and tracing—A review: Science of the Total Environment, v. 565, p. 8–27, https://doi.org/10.1016/j.scitotenv.2016.04.137.

Resh, V.H., Brown, A.V., Covich, A.P., Gurtz, M.E., Li, H.W., Minshall, G.W., Reice, S.R., Sheldon, A.L., Wallace, J.B., and Wissmar, R.C., 1988, The role of disturbance in stream ecology: Journal of the North American Benthological Society, v. 7, no. 4, p. 433–455, https://doi.org/10.2307/1467300.

Robertson, D.M., and Saad, D.A., 2019, Spatially referenced models of streamflow and nitrogen, phosphorus, and suspended-sediment loads in streams of the midwestern United States: U.S. Geological Survey Scientific Investigations Report 2019–5114, 74 p., including 5 appendixes, https://doi.org/10.3133/sir20195114.

Robertson, D.M., Saad, D.A., and Heisey, D.M., 2006, Present and reference concentrations and yields of suspended sediment in streams in the Great Lakes region and adjacent areas: U.S. Geological Survey Scientific Investigations Report 2006–5066, 35 p., https://doi.org/10.3133/sir20065066.

Rogers, H.A., Schmidt, T.S., Dabney, B.L., Hladik, M.L., Mahler, B.J., and Van Metre, P.C., 2016, Bifenthrin causes trophic cascade and altered insect emergence in mesocosms—Implications for small streams: Environmental Science & Technology, v. 50, no. 21, p. 11974–11983, https://doi.org/10.1021/acs.est.6b02761.

Rustad, L., Campbell, J., Dukes, J.S., Huntington, T., Lambert, K.F., Mohan, J., and Rodenhouse, N., 2012, Changing climate, changing forests—The impacts of climate change on forests of the northeastern United States and eastern Canada: U.S. Department of Agriculture, Forest Service, General Technical Report NRS-99, 56 p., accessed November 1, 2021, at https://www.fs.usda.gov/nrs/pubs/gtr/gtr_nrs99.pdf.

Savoy, P., and Harvey, J.W., 2020, Predicting light regime controls on primary productivity across CONUS river networks: Geophysical Research Letters, v. 48, no. 10, article e2020GL092149, 10 p., https://doi.org/10.1029/2020GL092149.

Schilling, K.E., Palmer, J.A., Bettis, E.A., III, Jacobson, P., Schultz, R.C., and Isenhart, T.M., 2009, Vertical distribution of total carbon, nitrogen and phosphorus in riparian soils of Walnut Creek, southern Iowa: CATENA, v. 77, no. 3, p. 266–273, https://doi.org/10.1016/j.catena.2009.02.006.

Schmadel, N.M., Harvey, J.W., Schwarz, G.E., Alexander, R.B., Gomez-Velez, J.D., Scott, D., and Ator, S.W., 2019, Small ponds in headwater catchments are a dominant influence on regional nutrient and sediment budgets: Geophysical Research Letters, v. 46, no. 16, p. 9669–9677, https://doi.org/10.1029/2019GL083937.

Sekely, A.C., Mulla, D.J., and Bauer, D.W., 2002, Streambank slumping and its contribution to the phosphorus and suspended sediment loads of the Blue Earth River, Minnesota: Journal of Soil and Water Conservation, v. 57, no. 5, p. 243–250, accessed November 1, 2021, at https://www.jswconline.org/content/57/5/243.

Simon, A., Dickerson, W., and Heins, A., 2004, Suspended-sediment transport rates at the 1.5-year recurrence interval for ecoregions of the United States—Transport conditions at the bankfull and effective discharge?: Geomorphology, v. 58, nos. 1–4, p. 243–262, https://doi.org/10.1016/j.geomorph.2003.07.003.

Skalak, K., and Pizzuto, J., 2010, The distribution and residence time of suspended sediment stored within the channel margins of a gravel-bed bedrock river: Earth Surface Processes and Landforms, v. 35, no. 4, p. 435–446, https://doi.org/10.1002/esp.1926.

Skalak, K.J., and Pizzuto, J., 2014, Reconstructing suspended sediment mercury contamination of a steep, gravel-bed river using reservoir theory: Environmental Geosciences, v. 21, no. 1, p. 17–35, https://doi.org/10.1306/eg.08151313007.

Stets, E.G., Sprague, L.A., Oelsner, G.P., Johnson, H.M., Murphy, J.C., Ryberg, K., Vecchia, A.V., Zuellig, R.E., Falcone, J.A., and Riskin, M.L., 2020, Landscape drivers of dynamic change in water quality of U.S. rivers: Environmental Science & Technology, v. 54, no. 7, p. 4336–4343, https://doi.org/10.1021/acs.est.9b05344.

Sutherland, A.B., Culp, J.M., and Benoy, G.A., 2010, Characterizing deposited sediment for stream habitat assessment: Limnology and Oceanography Methods, v. 8, no. 1, p. 30–44, https://doi.org/10.4319/lom.2010.8.30.

Taguchi, V.J., Olsen, T.A., Natarajan, P., Janke, B.D., Gulliver, J.S., Finlay, J.C., and Stefan, H.G., 2020, Internal loading in stormwater ponds as a phosphorus source to downstream waters: Limnology and Oceanography Letters, v. 5, no. 4, p. 322–330, https://doi.org/10.1002/lol2.10155.

Tian, Z., Zhao, H., Peter, K.T., Gonzalez, M., Wetzel, J., Wu, C., Hu, X., Prat, J., Mudrock, E., Hettinger, R., Cortina, A.E., Biswas, R.G., Kock, F.V.C., Soong, R., Jenne, A., Du, B., Hou, F., He, H., Lundeen, R., Gilbreath, A., Sutton, R., Scholz, N.L., Davis, J.W., Dodd, M.C., Simpson, A., McIntyre, J.K., and Kolodziej, E.P., 2021, A ubiquitous tire rubber-derived chemical induces acute mortality in coho salmon: Science, v. 371, no. 6525, p. 185–189, https://doi.org/10.1126/science.abd6951.

Turowski, J.M., Rickenmann, D., and Dadson, S.J., 2010, The partitioning of the total sediment load of a river into suspended load and bedload—A review of empirical data: Sedimentology, v. 57, p. 1126–1146.

U.S. Environmental Protection Agency [EPA], 1986, Quality criteria for water 1986 (“Gold Book”): U.S. Environmental Protection Agency, Office of Water Regulations and Standards, no. EPA 440/5-86-001, 395 p., accessed November 1, 2021, at https://www.epa.gov/sites/default/files/2018-10/documents/quality-criteria-water-1986.pdf.

U.S. Environmental Protection Agency [EPA], 1999, Protocol for developing sediment TMDLs (1st ed.): U.S Environmental Protection Agency, Office of Water, no. EPA 841-B-99-004, 143 p. [Available from https://www.epa.gov/nscep]

U.S. Environmental Protection Agency [EPA], 2016, National rivers and streams assessment 2008–2009—A collaborative survey: U.S. Environmental Protection Agency, Office of Water and Office of Research and Development, no. EPA/841/R-16/007, 119 p., accessed November 1, 2021, at http://www.epa.gov/national-aquatic-resource-surveys/nrsa [Also available at https://www.epa.gov/national-aquatic-resource-surveys/national-rivers-and-streams-assessment-2008-2009-report].

U.S. Environmental Protection Agency [EPA], 2017a, National Summary of State Information: U.S. Environmental Protection Agency, accessed January 5 2021, at https://iaspub.epa.gov/waters10/attains_nation_cy.control. [Also available at https://www.epa.gov/waterdata/attains].

U.S. Environmental Protection Agency [EPA], 2017b, National water quality inventory—Report to Congress: U.S. Environmental Protection Agency, no. EPA 841-R-16-011, 22 p., accessed January 5, 2021, at https://www.epa.gov/sites/default/files/2017-12/documents/305brtc_finalowow_08302017.pdf.

U.S. Environmental Protection Agency [EPA], 2017c, Water quality criteria, chap 3 *of* Water quality standards handbook: U.S. Environmental Protection Agency, Office of Water, no EPA 823-B-17-001, 28 p., accessed January 5, 2021, at https://www.epa.gov/wqs-tech/water-quality-standards-handbook.

U.S. Environmental Protection Agency [EPA], 2020, National rivers and streams assessment 2013–2014—A collaborative survey: U.S. Environmental Protection Agency, EPA 841-R-19-001, 65 p., accessed January 5, 2021, at https://www.epa.gov/system/files/documents/2021-10/nrsa_13-14_report_508_ci_2021-10-15.pdf.

Van Metre, P.C., and Fuller, C.C., 2009, Dual-core mass-balance approach for evaluating mercury and ^{210}Pb atmospheric fallout and focusing to lakes: Environmental Science & Technology, v. 43, no. 1, p. 26–32, https://doi.org/10.1021/es801490c.

Van Metre, P.C., and Horowitz, A.J., 2013, An 80-year record of sediment quality in the lower Mississippi River: Hydrological Processes, v. 27, no. 17, p. 2438–2448, https://doi.org/10.1002/hyp.9336.

Van Metre, P.C., and Mahler, B.J., 2004, Contaminant trends in reservoir sediment cores as records of influent stream quality: Environmental Science & Technology, v. 38, no. 11, p. 2978–2986, https://doi.org/10.1021/es049859x.

Van Metre, P.C., and Mahler, B.J., 2005, Trends in hydrophobic organic contaminants in urban and reference lake sediments across the United States, 1970–2001: Environmental Science & Technology, v. 39, no. 15, p. 5567–5574, https://doi.org/10.1021/es0503175.

Van Metre, P.C., and Mahler, B.J., 2010, Contribution of PAHs from coal-tar pavement sealcoat and other sources to 40 U.S. lakes: Science of the Total Environment, v. 409, no. 2, p. 334–344, https://doi.org/10.1016/j.scitotenv.2010.08.014.

Van Metre, P.C., Mahler, B.J., and Furlong, T., 2000, Urban sprawl leaves its PAH signature: Environmental Science & Technology, v. 34, no. 19, p. 4064–4070, https://doi.org/10.1021/es991007n.

Van Metre, P., Wilson, J.T., Fuller, C.C., Callender, E., and Mahler, B., 2004, Collection, analysis, and age-dating of sediment cores from 56 U.S. lakes and reservoirs sampled by the U.S. Geological Survey, 1992-2001: U.S. Geological Survey Scientific Investigations Report 2004–5184, 187 p., https://doi.org/10.3133/sir20045184.

Vannote, R.L., Minshall, G.W., Cummins, K.W., Sedell, J.R., and Cushing, C.E., 1980, The river continuum concept: Canadian Journal of Fisheries and Aquatic Sciences, v. 37, no. 1, p. 130–137, https://doi.org/10.1139/f80-017.

Wagner, S., Cawley, K.M., Rosario-Ortiz, F.L. and Jaffé, R., 2015, In-stream sources and links between particulate and dissolved black carbon following a wildfire: Biogeochemistry, v. 124, p. 145–161, https://doi.org/10.1007/s10533-015-0088-1.

Wainwright, J., Turnbull, L., Ibrahim, T.G., Lexartza-Artza, I., Thornton, S.F., and Brazier, R.E., 2011, Linking environmental régimes, space and time—Interpretations of structural and functional connectivity: Geomorphology, v. 126, nos. 3–4, p. 387–404, https://doi.org/10.1016/j.geomorph.2010.07.027.

Weltje, G.J., and Prins, M.A., 2007, Genetically meaningful decomposition of grain-size distributions: Sedimentary Geology, v. 202, no. 3, p. 409–424, https://doi.org/10.1016/j.sedgeo.2007.03.007.

Wohl, E., Cooper, D., Poff, L., Rahel, F., Staley, D., and Winters, D., 2007, Assessment of stream ecosystem function and sensitivity in the Bighorn National Forest, Wyoming: Environmental Management, v. 40, no. 2, p. 284–302, https://doi.org/10.1007/s00267-006-0168-z.

Wohl, E., Hall Jr., R.O., Lininger, K.B., Sutfin, N.A., and Walters, D.M., 2017, Carbon dynamics of river corridors and the effects of human alterations: Ecological Monographs, v. 87, no. 3, p. 379–409, https://doi.org/10.1002/ecm.1261.

Woznicki, S.A., Cada, P., Wickham, J., Schmidt, M., Baynes, J., Mehaffey, M., and Neale, A., 2020, Sediment retention by natural landscapes in the conterminous United States: Science of the Total Environment, v. 745, article 140972, 11 p., https://doi.org/10.1016/j.scitotenv.2020.140972.

Yamada, H., and Nakamura, F., 2002, Effect of fine sediment deposition and channel works on periphyton biomass in the Makomanai River, northern Japan: River Research and Applications, v. 18, no. 5, p. 481–493, https://doi.org/10.1002/rra.688.

Zhang, Q., Brady, D.C., Boynton, W.R., and Ball, W.P., 2015, Long-term trends of nutrients and sediment from the nontidal Chesapeake watershed—An assessment of progress by river and season: Journal of the American Water Resources Association, v. 51, no. 6, p. 1534–1555, https://doi.org/10.1111/1752-1688.12327.

Zhang, Q., Hirsch, R.M., and Ball, W.P., 2016, Long-term changes in sediment and nutrient delivery from Conowingo Dam to Chesapeake Bay—Effects of reservoir sedimentation: Environmental Science & Technology, v. 50, no. 4, p. 1877–1886, https://doi.org/10.1021/acs.est.5b04073.

Zhang, W., Xing, Y., Yu, L., Feng, H., and Lu, M., 2008, Distinguishing sediments from the Yangtze and Yellow Rivers, China—A mineral magnetic approach: The Holocene, v. 18, no. 7, p. 1139–1145, https://doi.org/10.1177/0959683608095582.

Chapter E

Freshwater Salinization—An Expanding Impairment of Aquatic Ecosystem Health

By Christopher H. Conaway, Nancy T. Baker, Judson W. Harvey, and Allen C. Gellis

Purpose and Scope

This chapter addresses knowledge gaps that, if filled, could improve predictions of aquatic ecosystem health as affected by freshwater salinization. The gaps identified in this chapter are not intended to be comprehensive but are instead focused on key opportunities for the U.S. Geological Survey (USGS) Water Resources Mission Area (WMA, https://www.usgs.gov/mission-areas/water-resources). Salinity effects on beneficial uses of water are not addressed in this chapter but are covered in Chapter B of Tesoriero and others (2024), “Addressing Salinity Challenges to the Beneficial Uses of Water,” the companion Open-File Report to this publication.

Statement of the Problem

Freshwater salinization is a primary concern for human health and aquatic life. The increasing salinity of freshwater resources in the United States poses a direct threat to ecological health and beneficial uses of that water on a national scale (Stets and others, 2020). Salinity is the sum of dissolved salts in water. However, unlike seawater, which has high concentrations of sodium (Na) and chloride (Cl) ions, freshwater tends to have several ions in various concentrations—for example, calcium (Ca), Cl, magnesium (Mg), potassium (K), and sulfate. In areas with hard or more alkaline water, Na and Cl may be in lower concentrations than Ca, Mg, bicarbonate, and sulfate. In contrast, pore water or groundwater in sedimentary basins, including many areas where energy development is presently concentrated, may have salinity that is similar to or greater than seawater, with major chemical composition varying based on terrestrial processes such as evaporation, water-rock interactions, and mixing of different water types, including mixing with groundwaters that contain relict seawater (Kharaka and Hanor, 2014). These disparate sources of ions contribute to the total salinity of water which can be inferred or measured in water by determining individual ion concentrations, specific conductance, or total dissolved solids (TDS)—which includes dissolved organic components.

Salinity and salinization of freshwater have long been leading water quality issues nationally and globally. The primary effects related to ecological health are related to lethal and sublethal effects on aquatic communities, loss of biodiversity, mobilization of contaminants, and effects on the riverine carbon cycle (Kaushal and others, 2021; Stets and others, 2020). In a U.S. Geological Survey (USGS) study of water-quality trends in United States rivers, Shoda and others (2019) determined that 26 percent of sites exceeded the U.S. Environmental Protection Agency’s (EPA’s) National Recommended Water-Quality Criteria stream aquatic life level of concern (LOC) for TDS. In a similar vein, in a study of Cl trends in northern United States urban streams (Corsi and others, 2015), 29 percent of sites studied exceeded the concentration for the EPA chronic water quality criteria of 230 milligrams per liter (mg/L) by an average of more than 100 individual days per year during 2006–2011. Moreover, recent analyses of USGS water quality data across the United States have identified a multi-decadal trend of increasing salinity in rivers and streams on a continental scale (Kaushal and others, 2018; Stets and others, 2020), focused particularly in urban-influenced watersheds.

Increases in alkalinity are also associated with salt pollution, although the environmental effects of alkalinization have received comparatively less attention and are perhaps less well understood than those of salinity (Kaushal and others, 2018). Many sources release alkaline salts like bicarbonate into the environment, including weathering of impervious surfaces, fertilizer and lime use in agriculture, mine drainage, irrigation runoff, and winter use of road salt. For example, Na in road salt can act to release the alkaline salts which then wash into freshwater ecosystems. Bicarbonate, the predominant form of dissolved inorganic carbon (DIC) in natural waters, originates primarily from watershed mineral weathering; however, human activities affect riverine bicarbonate fluxes, and we still cannot estimate the net effect on the global scale (Hamilton and Raymond, 2018).

The effects of freshwater salinization are a pervasive environmental issue and further study is needed for aggressive management strategies (Kaushal and others, 2018). Research is also needed to understand how changes in salinity, and in specific major ion concentrations, are related to specific water quality drivers and how those changes might be affecting aquatic ecology and ecosystem services (Stets and others, 2020) through toxicity or contaminant mobilization. More research is also crucial to adequately understand the effects of salinization on riverine carbon cycles (Kaushal and others, 2018).

Status of Knowledge and Key Limitations

The interrelated issues of salt ions and chemical, biological, and geologic parameters and consequences on the environment is called Freshwater Salinization Syndrome (Kaushal and others, 2021), and the key conceptual elements related to aquatic ecosystems are summarized in figure E1 and table E1. The general status of knowledge and information about salinity and related water-quality drivers is summarized in table E2. Many human activities contribute to increased salinity through a variety of processes, which complicates identification of the drivers of salinity increases or generalizes their effects on aquatic ecosystems. The predominant sources of salinity are well-known, and the sources driving observed changes include anthropogenic inputs of salt such as road salt, wastewater, water treatment, brine disposal, agricultural runoff; acceleration of natural weathering or water-rock interaction via acid rain, fertilizers, acid-mine drainage; and weathering of construction and manufacturing materials such as cement, lime, and concrete (Kaushal and others, 2018). Some of the environmental factors driving changes in salinity include climate change (for example, timing and amount of precipitation related to various kinds of runoff or chemical weathering), changes in water use (for example, surface water diversion, groundwater withdrawal, irrigation), changes in land-use and land cover, and sea level rise.

Many environmental ramifications of freshwater salinization are listed by Kaushal and others (2018), and include influencing the rates of coastal ocean acidification, the effects of toxicants, the water-sediment partitioning of toxic elements, decreasing soil stability and fertility, leaching and mobilization of nutrients, controlling the quality and release of organic matter from soils to streams, and altering aquatic ecosystem community structure. Some listed effects of alkalinization include changes in dissolved organic carbon (DOC) transported by rivers, changes in dissolved carbon dioxide, and influencing the distribution of invasive mussels. A recent analysis by Stets and others (2020) highlights the loss of stream biodiversity as one reason salinization is gaining attention as a worldwide problem; also because salinization can cause metals to desorb from streambed sediment. Other factors to consider related to salinity are ecosystem-related effects (for example, on mangrove wetlands, river delta communities, invasive species distribution, cyanobacteria community composition).

The ecosystem health gap analysis team for the WMA Water Quality Program identified five freshwater salinization ecological health impairments:

15. Community structure shifts related to toxicity or sensitivity to salinity,
16. Salt-tolerant invasive species,
17. Alteration of nutrient and organic matter cycling,
18. Mobilization of contaminants and bioactive elements, and
19. Alteration of soil properties and loss of structure.

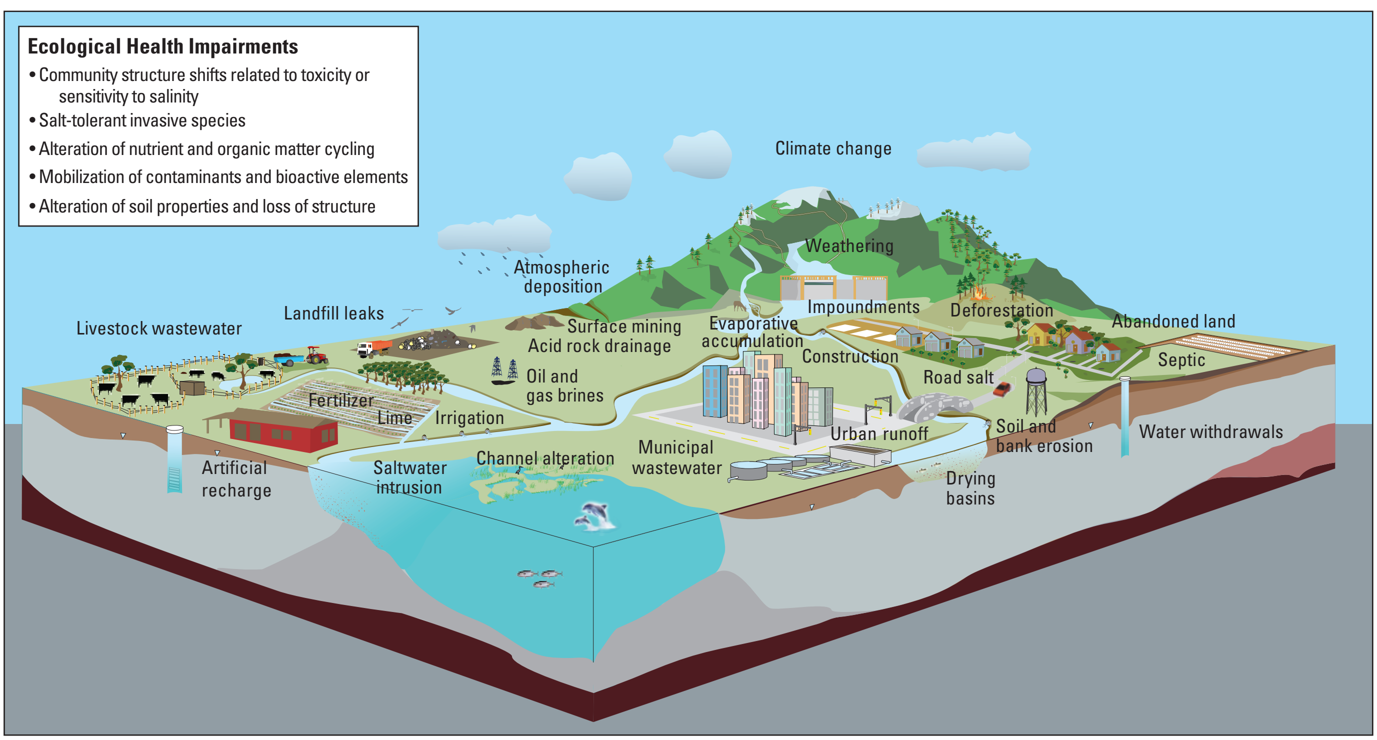


Figure E1. Diagram of sources and drivers of freshwater salinization with potential ecological health impairments.

Table E1. Summary table for freshwater salinity gap analysis for aquatic ecosystem health identified by the U.S. Geological Survey (USGS) and grouped by chemical salinization and ecosystem risks from salinization.

[CH_4, methane; H_2S, hydrogen sulfide]

What	Gap	Why	How
Chemical landscape of salinization			
Gap 1a Predicting and understanding changes	An understanding of event-based, seasonal, and long-term changes in salinity	Need to extrapolate measurements and model results over a wide range of hydrologic and climate variables	Monitor salinity with high frequency sensors. Develop long-term continuous data.
Gap 1b Loadings and pathways	Understanding of transport, storage, and elucidation of sources	Crucial for management, model prediction, and remediation	Watershed-ecosystem mass balance approach. Development and assessment of geochemical and isotopic tools for identifying sources.
Ecosystem risks from salinization			
Gap 2a Mobilization of chemical cocktails	Uncertainty regarding how different salt ions and mixtures across range of salinity affect biota, ecological communities, and ecosystem functions and services	Salinity causes mobilization of toxic chemicals and nutrients that affect biodiversity and ecosystem processes.	Survey of data on major ion ratios related to salinity in freshwater systems. Develop predictive models for geochemical water type in groundwater based on local geologic, hydrologic, and climatic conditions.
Gap 2b Effects of sea level rise	Complex geochemical modification of groundwater by seawater intrusion affecting community structure from microbes to forests	Ecosystem effects include microbial production and release of CH_4 or toxic H_2S, and salinity alteration of plant communities, carbon sequestration, and soil elevation change in coastal wetlands.	High-frequency continuous sensor output data investigation of salinity controls on dissolved organic matter processing, microbial products such as CH_4 and H_2S, resulting carbon burial and soil elevation change, including research on how saltwater intrusion affects soils (formation of plugs, dispersion of aggregates).
Gap 2c Changing community structure	Understanding of effects of salinization (for example, sea level rise and saltwater intrusion) on ecosystem health and community structure.	Changes affect coastal carbon sequestration, invasive species, and loss of plant communities anchoring coastal wetlands that transform nutrients and stabilize coastline.	Detailed (high frequency sensor) investigation of salinity controls on dissolved organic matter quantity and composition in coastal water, and on microbial products.

Because of the increasing concern regarding salinity related to increasing prevalence, ecological toxicity, and corrosion issues, there are major research and significant papers that continue to be published. Recent work on freshwater salinization by road salts and urbanization has been published by Moore and others (2020) on deicing; Kaushal and others (2018) on continental scale; Stets and others (2020) on landscape drivers in United States rivers; and Dugan and others (2017, 2020) on freshwater lakes. Recent work highlighting ecological effects includes Moore and others (2020) on conductivity and chloride exceedances of EPA aquatic life criteria in streams; and Hintz and Relyea (2017) work on responses of fish and zooplankton, and McCormick and others (2011) on responses of periphyton communities to freshwater salinization. Related to groundwater-surface water interaction, brackish groundwater assessments and information are presented by McMahon and others (2016) and in a USGS Professional Paper by Stanton and others (2017). Sprague and others (2019) presented recent work on changing salinity at multiple geographic scales using streamflow data and results from probabilistic and targeted monitoring, and Murphy and Sprague (2019) on the effects from streamflow trends and changes in watershed management. Work focusing on USGS Integrated Water Science (IWS) basins is presented by Rumsey and others (2017) on dissolved solids delivery to streams in the Upper Colorado River Basin.

Radionuclides

Saline water, either from road salts or from oil and gas development and production activities, has the potential to mobilize natural and contaminant radionuclides, such as radium-226 (^{226}Ra) and radium-228 (^{228}Ra) (Cozzarelli and

Table E2. Single-factor constituents of concern, drivers, and indicators of aquatic ecosystem health identified by the U.S. Geological Survey (USGS).

[Included are notations on sources and controlling factors, regions of concern, benchmarks for aquatic life and prevalence of exceedances, data availability, and references. CMC, criterion maximum concentration; CCC, criterion continuous concentration. IWS, Integrated Water Science; NAWQA, National Water Quality Assessment Project; EPA, U.S. Environmental Protection Agency; 303(d), Clean Water Act Section 303(d); TDS, total dissolved solids; LOC, level of concern; mg/L, milligrams per liter; %, percent; NORM, naturally occurring radioactive materials; TENORM, technologically enhanced naturally occurring radioactive materials; U-Th, uranium-thorium.]

Category, constituent, or driver	Source areas, controlling factors, and (or) value as an indicator	Areas or regions of concern	Benchmarks for aquatic life and information about exceedances	Data availability for analysis
Salinity[1]	Road salt, groundwater extraction, mining, oil and gas produced water, agricultural return flows, sea level rise, surface water diversion, stormwater, urban runoff and wastewater discharge, landscape disturbance, drinking water chlorination (Anning and Flynn 2014)	National, global, and includes USGS IWS basins.	See TDS, chloride, and conductivity below.	See TDS, chloride, and conductivity below.
TDS[2]	Road salt, groundwater extraction, mining, oil and gas produced water, agricultural return flows, sea level rise, surface water diversion, stormwater, urban runoff and wastewater discharge, landscape disturbance, drinking water chlorination (Anning and Flynn 2014).	National, global, and includes USGS IWS basins.	EPA National recommended water criteria stream aquatic life: LOC 500 mg/L; 26% of 208 continental United States stream sites exceeded LOC (Shoda and others, 2019).	Anning and Flynn 2014; Stanton and others, 2017. USGS discrete data (USGS, 2022).
Chloride	Municipal and industrial discharges, septic systems, and road-salt runoff.	National, global, and includes USGS IWS basins, especially areas with increasing urban land use.	Federal EPA CMC is 860 mg/L; CCC is 230 mg/L. Corsi and others (2015) found the CCC exceeded in 29% of major cities investigated	USGS discrete data (USGS, 2022)
Conductivity[3]	Used to estimate salinity/TDS.	Increasing in all human-dominated landscapes, that is, in streams in urban and agricultural areas, and areas with a mix of the two (Stets and others, 2020)		Fanelli and others, 2019. USGS discrete data (USGS, 2022). USGS real-time data (https://waterwatch.usgs.gov/wqwatch/?pcode=00095). USGS National Water Quality Watch (https://waterdata.usgs.gov/nwis/current/?type=quality&group_key=NONE).
Radionuclides[4]	Radionuclides may be important in certain environments/regions (Szabo and others, 2020). NORM and TENORM an issue in oil fields and related waste disposal (Cozzarelli and others, 2017; McDevitt and others, 2019).	Groundwater from naturally U-Th rich rock, contamination from oil and gas exploration and extraction and waste disposal.	Not captured in EPA's recommended aquatic life criteria.	USGS produced water database (https://eerscmap.usgs.gov/pwapp/) USGS NAWQA (https://www.usgs.gov/programs/national-water-quality-program/national-water-quality-assessment-project-nawqa) (Szabo and others, 2020).

[1]Strictly speaking is only dissolved salts, but often used interchangeably with TDS—see entry below.

[2]All dissolved material, can include organic solutes.

[3]Specific conductance.

[4]Radium-228, Radium-226.

others, 2017; McDevitt and others, 2019). The geochemical mobility of Ra is often controlled by either sorption or co-precipitation with sulfate or carbonate minerals. For example, elevated sediment radium from co-precipitation with carbonate was observed downstream of produced water discharge in Wyoming streams (McDevitt and others, 2019). Alternatively, mobilization due to desorption is shown in a study on the mobilization of radium and radon by deicing salt contamination of groundwater under a parking lot in Connecticut that concluded that salt contamination of groundwater could increase the potential for human exposure to these radioactive and carcinogenic elements (McNaboe and others, 2017). High concentrations of naturally occurring Ra are known to cause human health effects (EPA, 2000). However, there is a knowledge gap on the effects of water quality shifts (dilution or acidification) on Ra distribution downstream of contaminated sites (Cozzarelli and others, 2017; McDevitt and others, 2019), and the health effects of Ra on wildlife are not well known (McDevitt and others, 2019). Thus, to understand the potential for long-term downstream contamination from mobilized radionuclides, there is the need to study the environmental behavior of these chemicals along complex hydrologic flowpaths (Kaushal and others, 2021). Further discussion of the significance of environmental radionuclides can be found in the companion report, chapter C “Geogenic Water-Quality Effects on Beneficial Uses of Water” (Tesoriero and others, 2024).

Knowledge Gaps in Salinity Drivers of Ecosystem Health

Salinization is increasing in many parts of the United States and globally and is a complicated emerging problem for ecosystem health (Kaushal and others, 2021). Although salinity is decreasing in some areas, which may reflect successful mitigation strategies (Rumsey and others, 2017) or salinity cycles related to changes in precipitation (Tillman and others, 2019), increases are evident especially in urban areas and dryland environments (Stets and others, 2020). For USGS Water Mission Resources Area (WMA) research, we divide knowledge gaps into needs for increased understanding into two broad classes of gaps:

1. Defining the chemical landscape of salinization, which includes:
    a. predicting and understanding changes in salinity, and
    b. salinity loadings and pathways.
2. Evaluating ecosystem risks from salinization, which include:
    a. risks related to salinity mobilization of “chemical cocktails,”
    b. effects of sea level rise on coastal ecosystems, and
    c. the effects of salinization on changing community structure (from microbes to HABs to invasive species).

We present these gaps in detail below and provide a summary in table E1.

Gap 1. Defining the Chemical Landscape of Salinization

The first class of gaps in defining the chemical landscapes of salinization include:

Gap 1a. Predicting and Understanding Changes in Salinity

Decadal-scale salinization has been well-documented in arid, semi-arid, humid, and urban regions across the United States and globally (Kaushal and others, 2021; Stets and others, 2020). Some of the major gaps in understanding the drivers of salinity changes include the role of seasonal trends and an understanding of the landscape processes and broad regional changes that affect water quality. These changes can be important, such as in the case of increased salinity during low-flow conditions when biotas are most sensitive to changes in water quality (Stets and others, 2020). Climate driven changes include reduction in precipitation, increases in aridity, and other long-term changes contributing to salinization include increasing urbanization and water use (Vengosh, 2014). In addition, more information is needed on how storm and snow events influence salinity and related contaminant load across a variety of landscapes (Corsi and others, 2015; Kaushal and others, 2021). Better understanding of these short-term and long-term drivers should allow us to better predict and manage salinity in the future. Consequently, we propose that research should be carried out by focusing on target basins to address these questions:

- How might the rates of supply from salinity sources change due to climate change?
- What event, seasonal or interannual trends of salinity, exist in river and lake environments (including storm events, droughts, snow events, wind-blown dust from exposed shorelines)?
- How might the rates of supply from salinity sources change due to land use change including changes in groundwater pumping, irrigation, and energy development?
- How might the rates and supply from salinity sources change due to infrastructure change (flow management, water diversions, interbasin transfers)?
- Where and at what rate are anthropogenic sources—such as road salt, liming and fertilizer, and septic systems—increasing salinity in the unsaturated zone and shallow groundwater causing mobilization of chemicals in the soil

profile that may ultimately be carried to surface-water aquatic ecosystems?

- How is salinization of rivers and lakes related to variable inputs from runoff and groundwater across seasonal to decadal time scales?

For these events, seasonal, interannual and long-term trends, work is required using high-frequency continuous sensor output data for salinity, preferably across a range of land use types and precipitation patterns (rain, snow, snow melt, arid, humid, urban, agriculture) combined with traditional streamflow monitoring and new approaches to modeling and links to other geochemical data (Kaushal and others, 2021). Long-term high frequency data would allow for the determination of peaks, response time, and hysteresis in salinity versus flow across different time scales from storm events to interannual trends. These data could also be useful to determine the time scale of exceedances of water quality criteria, and longer records of these data could be used to determine whether there has been an increase or decrease in the number of days exceeding those criteria. Deliverables for this work should be high-frequency continuous sensor data for target basins that can be used to better understand and predict natural and human-accelerated salinization on short-term to decadal scales, and an interpretation of the processes driving these changes. Beyond adopting high-frequency continuous sensor data approaches, some basic questions of seasonality and the relationship to streamflow could be explored in many places with existing and extensive discrete data when combined with modeling efforts such as weighted regressions on time, streamflow, and season (Oelsner and others, 2017).

Gap 1b. Salinity Loadings and Pathways

Qualitative knowledge of loading, response time, and hydrologic flowpaths of salinity from existing sources is crucial to understanding and managing salinization of aquatic ecosystems. Establishing loadings and pathways is essential for determining the legacy response time of current salinity loads, as well as predicting the results of increasing loads. Salt from atmospheric deposition, evaporation of surface water, or anthropogenic salinity sources can accumulate in water and soils in the saturated or unsaturated zone and later can be flushed downward or laterally. The flushing can be caused by changes in land use such as removing vegetation or changing vegetation type (for example, natural to cropland), or changes in hydrologic budget through increased rainfall, irrigation, or even sea level rise. Storage and flushing of salinity are well-documented in dryland environments (Vengosh, 2014), but less so in urban areas or basins with anthropogenic salinization (Lax and Peterson, 2008; Ledford and others, 2016).

To address this gap, we support following the recommendation of Kaushal and others (2021) to develop a watershed-ecosystem approach. The initial screening is a mass balance of TDS at the regional to national scale to better understand how different hydrogeologic settings and land uses affect river loads. Next is a partitioning of individual major components (for example, Na, Cl, sulfate, bicarbonate) for target watersheds such as the USGS IWS basins; including an evaluation of “hot spots,” such as near roadways, wildfire burn areas, wastewater discharge, urban areas, resource development and extraction, and groundwater. We note that refining the mass balance of TDS to the level of major components may be limited by available data and requires new data collection.

To complement this approach, forensic work on determining the relative contributions of salinity sources could be carried out. Where there are multiple sources of salinity to a system, the integration of multiple chemical and isotopic tracers is required to distinguish between these sources (Vengosh, 2014). Common tracers for salinity sources include chemical ratios (for example, Na/Cl, Br/Cl, B/Cl, Ca/Cl, SO_4/Cl) and isotopic ratios (for example, $\delta^{18}O$ and $\delta^{2}H$ in H_2O, $\delta^{11}B$, $\delta^{34}S$, $\delta^{34}S$ and $\delta^{18}O$ in SO_4, $^{36}Cl/Cl$, $^{129}I/^{127}I$, $^{87}Sr/^{86}Sr$). To quantitatively relate sources of salinity to water quality observations and predictions in target basins, projects could be pursued to evaluate data availability and application of these geochemical tools. Deliverables for projects could include identification of the best combination or integration of tracers in these systems, a compilation of available data, and potential tracers for reuse water. Other potential work identified by USGS to provide better quantification of the sources and causal factors includes:

- Examination or acquisition of road-salt use data to attribute cause and determine if “legacy” road salt is a concern,
- Determining atmospheric dry (aerosol or aeolian dust) deposition rates of salt to determine the relative importance to wet deposition rates, and
- Compiling TDS estimates from wastewater to better understand its role in salinization.

Gap 2. Evaluating Ecosystem Risks from Salinization

The second class of gaps in evaluating ecosystem risks from salinization include:

Gap 2a. Salinity Mobilization of Chemical Cocktails (Mixtures)

There is much uncertainty regarding how different salt ions and mixtures across a range of salinity affect biota, ecological communities, and ecosystem functions and services (Kaushal and others, 2021). Research is needed to understand how increases in salinity, and in specific major ion concentrations, might be affecting aquatic ecology and ecosystem services (Stets and others, 2020) through toxicity or contaminant mobilization. Much of the work on the environmental effects of salinization has focused on Cl; but different components of salinity—Na, Mg, Ba, bicarbonate, sulfate, silica—are recognized to have different effects on the health of aquatic systems. Examples include (1) different salts influence toxicity to aquatic organisms (Kaushal and others, 2018); (2) mobilization of geogenic contaminants such as fluoride (F), arsenic (As), B, and Ra by salinization (Vengosh, 2014); and (3) salinization can cause leaching and mobilization of bioreactive elements (carbon [C], nitrogen [N], phosphorus [P]) from soil to water in streams (Kaushal and others, 2018). A survey of the importance and availability of data on major ion ratios related to salinity in freshwater systems would be beneficial to understanding the effects of salinization. In addition, predictive models for geochemical water types in groundwater that are based on local geologic, hydrologic, and climatic conditions could be developed. There is crossover in examining major ion chemistry controlling speciation with the presentation in chapter C "Geogenic Water-Quality Effects on Beneficial Uses of Water" in the companion report (Tesoriero and others, 2024). Consequently, we propose:

- Developing prediction capability to determine major ion ratios and effects on beneficial uses via corrosion, mobilization of contaminants, and suitability for use;
- Examination of the role of salinity in the prediction of health-related geogenics (for example, F, As, Se, B, Ra); and
- Inclusion in models for the prediction of water types based on geochemical processes (for example, base cation exchange, freshening, generation of dissolved inorganic carbon [DIC] by oxidation of organic matter).

Gap 2b. Effects of Sea Level Rise on Coastal Ecosystems

The effects of sea level rise and saltwater intrusion on ecosystem health and community structure represents another important research area (Vengosh, 2014; Kaushal and others, 2021). The complex geochemical modification of groundwater by seawater intrusion and displacement is considered above under sections Gap 1b "Salinity Loadings and Pathways" and Gap 2a "Salinity Mobilization of Chemical Cocktails (Mixtures)." Research is also crucial for determining how saltwater intrusion affects soils (formation of plugs, dispersion of aggregates). Ecosystem effects include modification of microbial community structure resulting in changes in production and release of CH_4 or toxic H_2S. Salinity alteration of DOC export, plant community structure, and coastal wetland carbon sequestration represents another important research area (Kaushal and others, 2021). Research specific to USGS WMA National Water Quality Program (NWQP) could include detailed (high-frequency continuous sensor output data) investigation of salinity controls on dissolved organic matter quantity and composition in coastal water, and on microbial products such as CH_4 and H_2S, which can also be determined with continuous sensors.

Gap 2c. The Effects of Salinization on Changing Community Structure (From Microbes to Harmful Algal Blooms to Invasive Species)

There are major research gaps and management questions on the topic of salinization and ecosystem effects (Vengosh, 2014; Kaushal and others, 2021). These gaps include both knowledge of direct effects on organisms and biodiversity through toxicity related to chloride, as well as indirect effects such as the alteration of microbial community structure through mobilization of nutrients and contaminants related to salinization (Kaushal and others, 2021). Salinization of surface water can trigger harmful algal blooms (HABs) with profound effects on fish, salamanders, and mussels (Vengosh, 2014). Salinization also has effects on the distribution and success of salt-tolerant invasive species (Kaushal and others, 2021). Research gaps on HABs and invasive species are covered in other programs within USGS and WMA; however, as described above under Gap 1a "Predicting and Understanding Changes in Salinity," high-frequency continuous sensor output data for salinity, preferably across a range of land use types and precipitation patterns (rain, snow, snow melt, arid, humid, urban, agriculture) combined with new approaches to modeling and links to other geochemical data could greatly contribute to research on these topics.

Priorities and Timelines for Addressing Gaps

Priorities

Gap 1a. Predicting and Understanding Changes in Salinity

This gap has high value scientifically both regionally and nationally, but is given number 2 rank in priority because this is a "long term" problem compared to the more immediate needs addressed in Gap 1b.

Gap 1b. Salinity Loadings and Pathways

This work provides information for management in the "now", and there is high value in water-stressed areas and at-risk areas.

Gap 2a. Salinity Mobilization of Chemical Cocktails (Mixtures)

There is good potential for process understanding inclusion into models, but effort may require substantial geochemical expertise. The chemistry and concepts are complex, and the value of data may be specific to USGS Integrated Water Science (IWS) basins but the knowledge gained is applicable across many aquatic systems.

Gaps 2b and 2c. Sea Level Rise, Salinization, and Changing Community Structure

The work is high value within areas, but knowledge transfer to other IWSs may be low because ecosystem communities are somewhat unique and therefore the knowledge gained is not widely applicable. In addition, the factors and drivers extend beyond salinity.

Timelines

Near-Term (2–5 Years)

Approaches to fill knowledge gaps that fall into a near-term (2-year) level of implementation consist of plans for the development and identification or deployment of high-frequency continuous sensor output data for (1) salinity in existing IWSs, (2) the development of lists and methods for forensic tools for salinity sources in existing IWSs, and (3) the development of data collection and management plans. Other approaches in the near-term are related to a watershed-ecosystem type approach in IWSs and include developing mass balance of TDS in IWSs and identification and evaluation of salinity "hot spots" in those IWSs, such as near roadways, wildfire burn areas, wastewater discharge, urban areas, resource development and extraction, and groundwater.

Mid- to Long-Term (5–10 Years)

Approaches to fill knowledge gaps that fall into mid- (5-year) to long-term (10-year) implementation timeframes are (1) the development of long-term ecological data sets, (2) refining the focus in watershed-ecosystem mass balance approaches to individual major components of salinity, (3) developing and assessing results of management actions, and (4) refining model predictions with long-term, high-frequency sensor data.

References Cited

Anning, D.W, and Flynn, M.E., 2014, Dissolved-solids sources, loads, yields, and concentrations in streams of the conterminous United States: U.S. Geological Survey Scientific Investigations Report 2014–5012, 101 p., https://doi.org/10.3133/sir20145012.

Corsi, S.R., De Cicco, L.A., Lutz, M.A., and Hirsch, R.M., 2015, River chloride trends in snow-affected urban watersheds—Increasing concentrations outpace urban growth rate and are common among all seasons: Science of the Total Environment, v. 508, p. 488–497, https://doi.org/10.1016/j.scitotenv.2014.12.012.

Cozzarelli, I.M., Skalak, K.J., Kent, D.B., Engle, M.A., Benthem, A., Mumford, A.C., Haase, K., Farag, A., Harper, D., Nagel, S.C., Iwanowicz, L.R., Orem, W.H., Akob, D.M., Jaeschke, J.B., Galloway, J., Kohler, M., Stoliker, D.L., and Jolly, G.D., 2017, Environmental signatures and effects of an oil and gas wastewater spill in the Williston Basin, North Dakota: Science of the Total Environment, v. 579, p. 1781–1793, https://doi.org/10.1016/j.scitotenv.2016.11.157.

Dugan, H.A., Bartlett, S.L., Burke, S.M., Doubek, J.P., Krivak-Tetley, F.E., Skaff, N.K., Summers, J.C., Farrell, K.J., McCullough, I.M., Morales-Williams, A.M., Roberts, D.C., Ouyang, Z., Scordo, F., Hanson, P.C., and Weathers, K.C., 2017, Salting our freshwater lakes: Proceedings of the National Academy of Sciences, v. 114, no. 17, p. 4453–4458, https://doi.org/10.1073/pnas.1620211114.

Dugan, H.A., Skaff, N.K., Doubek, J.P., Bartlett, S.L., Burke, S.M., Krivak-Tetley, F.E., Summers, J.C., Hanson, P.C., and Weathers, K.C., 2020, Lakes at risk of chloride contamination: Environmental Science & Technology, v. 54, no. 11, p. 6639–6650, https://doi.org/10.1021/acs.est.9b07718.

Fanelli, R.M., Sekellick, A.J., and Moore, J., 2019, Discrete and high-frequency chloride (Cl) and specific conductance (SC) data sets and Cl-SC regression equations used for analysis of 93 USGS water quality monitoring stations in the eastern United States: U.S. Geological Survey data release, https://doi.org/10.5066/P9YN2QST.

Hamilton, S.K., and Raymond, P.A., 2018, Anthropogenic influences on riverine fluxes of dissolved inorganic carbon to the oceans: Limnology and Oceanography Letters, v. 3, no. 3, p. 143–155, https://doi.org/10.1002/lol2.10069.

Hintz, W.D., and Relyea, R.A., 2017, A salty landscape of fear—Responses of fish and zooplankton to freshwater salinization and predatory stress: Oecologia, v. 185, no. 1, p. 147–156, https://doi.org/10.1007/s00442-017-3925-1.

Kaushal, S.S., Likens, G.E., Pace, M.L., Reimer, J.E., Maas, C.M., Galella, J.G., Utz, R.M., Duan, S., Kryger, J.R., Yaculak, A.M., Boger, W.L., Bailey, N.W., Haq, S., Wood, K.L., Wessel, B.M., Park, C.E., Collison, D.C., Aisin, B.Y.I., Gedeon, T.M., Chaudhary, S.K., Widmer, J., Blackwood, C.R., Bolster, C.M., Devilbiss, M.L., Garrison, D.L., Halevi, S., Kese, G.Q., Quach, E.K., Rogelio, C.M.P., Tan, M.L., Wald, H.J.S., and Woglo, S.A., 2021, Freshwater salinization syndrome—From emerging global problem to managing risks: Biogeochemistry, v. 154, no. 2, p. 255–292, https://doi.org/10.1007/s10533-021-00784-w.

Kaushal, S.S., Likens, G.E., Pace, M.L., Utz, R.M., Haq, S., Gorman, J., and Grese, M., 2018, Freshwater salinization syndrome on a continental scale: Proceedings of the National Academy of Sciences, v. 115, no. 4, p. E574–E583, https://doi.org/10.1073/pnas.1711234115.

Kharaka, Y.K., and Hanor, J.S., 2014, Deep fluids in sedimentary basins, chap 7.14 *of* volume 7, Surface and groundwater, weathering and soils, *in* Holland, H.D., and Turekian, K.K., eds., Treatise on Geochemistry (2d ed.): Oxford, Elsevier, p. 471–515.

Lax, S., and Peterson, E.W., 2008, Characterization of chloride transport in the unsaturated zone near salted road: Environmental Geology, v. 58, no. 5, p. 1041–1049, at https://doi.org/10.1007/s00254-008-1584-6.

Ledford, S.H., Lautz, L.K., and Stella, J.C., 2016, Hydrogeologic processes impacting storage, fate, and transport of chloride from road salt in urban riparian aquifers: Environmental Science & Technology, v. 50, no. 10, p. 4979–4988, https://doi.org/10.1021/acs.est.6b00402.

McCormick, P.V., Harvey, J.W., and Crawford, E.S., 2011, Influence of changing water sources and mineral chemistry on the Everglades ecosystem: Critical Reviews in Environmental Science and Technology, v. 41, no. sup1, p. 28–63, https://doi.org/10.1080/10643389.2010.530921.

McDevitt, B., McLaughlin, M., Cravotta, C.A., Ajemigbitse, M.A., Van Sice, K.J., Blotevogel, J., Borch, T., and Warner, N.R., 2019, Emerging investigator series—Radium accumulation in carbonate river sediments at oil and gas produced water discharges—Implications for beneficial use as disposal management: Environmental Science—Processes & Impacts, v. 21, no. 2, p. 324–338, https://doi.org/10.1039/C8EM00336J.

McMahon, P.B., Böhlke, J.K., Dahm, K.G., Parkhurst, D.L., Anning, D.W., and Stanton, J.S., 2016, Chemical considerations for an updated national assessment of brackish groundwater resources: Groundwater, v. 54, no. 4, p. 464–475, https://doi.org/10.1111/gwat.12367.

McNaboe, L.A., Robbins, G.A., and Dietz, M.E., 2017, Mobilization of radium and radon by deicing salt contamination of groundwater: Water, Air, & Soil Pollution, v. 228, article 94, 9 p., https://doi.org/10.1007/s11270-016-3227-y.

Moore, J., Fanelli, R.M., and Sekellick, A.J., 2020, High-frequency data reveal deicing salts drive elevated specific conductance and chloride along with pervasive and frequent exceedances of the U.S. Environmental Protection Agency Aquatic Life Criteria for chloride in urban streams: Environmental Science & Technology, v. 54, no. 2, p. 778–789, https://doi.org/10.1021/acs.est.9b04316.

Murphy, J., and Sprague, L., 2019, Water-quality trends in US rivers—Exploring effects from streamflow trends and changes in watershed management: Science of the Total Environment, v. 656, p. 645–658, https://doi.org/10.1016/j.scitotenv.2018.11.255.

Oelsner, G.P., Sprague, L.A., Murphy, J.C., Zuellig, R.E., Johnson, H.M., Ryberg, K.R., Falcone, J.A., Stets, E.G., Vecchia, A.V., Riskin, M.L., De Cicco, L.A., Mills, T.J., and Farmer, W.H., 2017, Water-quality trends in the Nation's rivers and streams, 1972–2012—Data preparation, statistical methods, and trend results: U.S. Geological Survey Scientific Investigations Report 2017–5006, 136 p., 8 appendixes, https://doi.org/10.3133/sir20175006.

Rumsey, C.A., Miller, M.P., Schwarz, G.E., Hirsch, R.M., and Susong, D.D., 2017, The role of baseflow in dissolved solids delivery to streams in the Upper Colorado River Basin: Hydrological Processes, v. 31, no. 26, p. 4705–4718, https://doi.org/10.1002/hyp.11390.

Shoda, M.E., Sprague, L.A., Murphy, J.C., and Riskin, M.L., 2019, Water-quality trends in U.S. rivers, 2002 to 2012—Relations to levels of concern: Science of the Total Environment, v. 650, part 2, p. 2314–2324, https://doi.org/10.1016/j.scitotenv.2018.09.377.

Sprague, L.A., Mitchell, R.M., Pollard, A.I., and Falcone, J.A., 2019, Assessing water-quality changes in US rivers at multiple geographic scales using results from probabilistic and targeted monitoring: Environmental Monitoring and Assessment, v. 191, article 348, 12 p., https://doi.org/10.1007/s10661-019-7481-5.

Stanton, J.S., Anning, D.W., Brown, C.J., Moore, R.B., McGuire, V.L., Qi, S.L., Harris, A.C., Dennehy, K.F., McMahon, P.B., Degnan, J.R., and Böhlke, J.K., 2017, Brackish groundwater in the United States: U.S. Geological Survey Professional Paper 1833, 185 p., https://doi.org/10.3133/pp1833.

Stets, E.G., Sprague, L.A., Oelsner, G.P., Johnson, H.M., Murphy, J.C., Ryberg, K., Vecchia, A.V., Zuellig, R.E., Falcone, J.A., and Riskin, M.L., 2020, Landscape drivers of dynamic change in water quality of U.S. rivers: Environmental Science & Technology, v. 54, no. 7, p. 4336–4343, https://doi.org/10.1021/acs.est.9b05344.

Szabo, Z., Stackelberg, P.E., Cravotta, C.A., III, 2020, Occurrence and geochemistry of lead-210 and polonium-210 radionuclides in public-drinking-water supplies from principal aquifers of the United States: Environmental Science & Technology, v. 54, no. 12, p. 7236–7249, https://doi.org/10.1021/acs.est.0c00192.

Tesoriero, A.J., Erickson, M.L., Conaway, C.H., Tomaszewski, E.J., and Green, C.T., eds., 2024, Knowledge gaps and opportunities for understanding water quality processes affecting water availability for beneficial uses in the conterminous United States: U.S. Geological Survey Open-File Report 2023–1086, 81 p., https://doi.org/10.3133/ofr20231086.

Tillman, F.D., Coes, A.L., Anning, D.W., Mason, J.P., and Coplen, T.B., 2019, Investigation of recent decadal-scale cyclical fluctuations in salinity in the lower Colorado River: Journal of Environmental Management, v. 235, p. 442–452, https://doi.org/10.1016/j.jenvman.2019.01.072.

U.S Environmental Protection Agency [EPA], 2000, National primary drinking water regulations; Radionuclides [final rule]: Federal Register, v. 65, no. 236, p.76708–76753, accessed January 5, 2021, at https://www.federalregister.gov/documents/2000/12/07/00-30421/national-primary-drinking-water-regulations-radionuclides-final-rule.

U.S. Geological Survey [USGS], 2022, USGS water data for the Nation: U.S. Geological Survey National Water Information System database, accessed November, 2022, at http://dx.doi.org/10.5066/F7P55KJN.

Vengosh, A., 2014, Salinization and saline environments, chap. 9.09 *in* Lollar, B.S., Volume 9 *of* Holland, H.D., and Turekian, K.K., Treatise on geochemistry, 35 p., https://doi.org/10.1016/B0-08-043751-6/09051-4.

Moffett Field Publishing Service Center
Manuscript approved October 12, 2023
Edited by Kathryn Pauls
Illustration support by Kimber Petersen
Layout by Cory Hurd

USGS

Harvey and others, editors—**Knowledge Gaps and Opportunities in Water-Quality Drivers of Aquatic Ecosystem Health**—Open-File Report 2023–1085

ISSN 2331-1258 (online)
https://doi.org/10.3133/ofr20231085